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Mineral species as functions of *p*H and oxidation-reduction potentials, with special reference to the zone of oxidation and secondary enrichment of sulphide ore deposits

Robert M. Garrels*

Contribution from Northwestern University

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ABSTRACT

A series of diagrams has been prepared showing some stability and solubility relations among lead, zinc, and copper minerals found in the zones of oxidation and secondary enrichment of sulphide ore deposits. The stability and solubility relations are expressed as functions of *p*H and oxidation-reduction potential. These diagrams show theoretical equilibrium relations, and are sufficiently similar to relations found in the natural system to imply that the synthetic approach may be useful in the interpretation of field relations. The diagrams suggest the existence of relationships not previously reported, and provide plausible explanations for some known phenomena. A definition of the boundary between the "zone of oxidation" and "zone of secondary enrichment" is proposed.

Introduction

Many natural chemical systems are characterized by continuous chemical activity, even though the environment is one of essentially constant temperature and pressure. In many such systems, the reactions involved are characterized almost entirely by the *p*H and the oxidation-reduction potential (*Eh*) of the environment (Mason, 1949; Krumbein and Garrels, 1952; Huber and Garrels, 1953). Only at 25°C and atmospheric pressure are data available for even semi-quantitative handling of such systems; fortunately many important natural systems do not deviate so far from these conditions that the relations at 25° are not applicable to them. It is possible, if certain reasonable assumptions concerning composition of the system are made, to calculate fields of stability of various minerals as functions of *p*H and *Eh*. These predicted equilibrium relations can then be compared to natural occurrences, and can be investigated experimentally. From investigation of a sufficient number of mineral occurrences, some information should be gleaned on the validity of this approach, and perhaps some insight can be gained as to occurrences that actually represent chemical equilibrium. Conversely, implications should accumulate on minerals that persist metastably, and on the kinetics of many reactions of geologic importance.

In the paper, some of the mineral relations in the zones of oxidation and secondary enrichment of sulphide ore deposits are discussed as examples of the application of this technique to a particular environment.

Generalized Chemistry of the Zone of Oxidation and Secondary Enrichment

A typical primary ore deposit might consist of galena (PbS), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$) disseminated in a limestone or igneous rock matrix. This association is stable in the environment found beneath the ground water table—mildly alkaline and moderately reducing—and remains without change

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indefinitely. But when erosion exposes such a deposit at the surface, oxidation and solution take place. Lead remains at or near the surface, but the sulphide is converted to sulphate or carbonate. Zinc goes into solution and tends to move downward; some of it remains near the surface as the silicate or as the carbonate, but most seems to move entirely away from the original deposit. The behaviour of copper is perhaps most complex; it moves downward, precipitating en route in a wide variety of minerals. Among them are two basic carbonates; two oxides; a silicate; and two sulphides. Some pertinent information is summarized in the following table.

Table 1. *Major minerals of lead, zinc, and copper in the zone of oxidation and secondary enrichment*

Mineral	*Composition*
Galena	PbS } Primary minerals; sphalerite
Sphalerite	ZnS } and chalcopyrite commonly
Chalcopyrite	$CuFeS_2$ } entirely removed
Cerussite	$PbCO_3$
Anglesite	$PbSO_4$
Calamine	$Zn_2SiO_4.nH_2O$
Smithsonite	$ZnCO_3$
Cuprite	Cu_2O
Tenorite	CuO
Malachite	$Cu_2(OH)_2CO_3$
Azurite	$Cu_3(OH)_2(CO_3)_2$
Chalcocite	Cu_2S
Covellite	CuS
Chrysocolla	$CuSiO_3.nH_2O$

Very broadly, the changes in the zone of oxidation involve freeing the metal ions by oxidation of sulphide to sulphate, and reprecipitation of the metals by reaction with carbonate, hydroxyl, silicate, or sulphate ions. For copper, additional reactions occur; some copper travels downward to the water table, and is re-precipitated nearby as a sulphide.

DEPENDENCE OF METAL ION ACTIVITY ON *p*H AND OXIDATION POTENTIAL

The activity products of many of the compounds in Table 1 are known at 25°C, consequently the maximum activity of the metal ions can be calculated if the activity of the anions is known.

Assignment of a *p*H value automatically determines the activity of hydroxyl ions and thus also specifies the activity of the metal ions in the precipitation of hydroxides or oxides.

Also assignment of a *p*H value restricts the carbonate ion concentration within rather narrow limits. When ores are oxidized in limestone the free acid developed during oxidation reacts with the limestone and the solutions developed are saturated with CO_2. In igneous rocks the amount of CO_2 in solution is more difficult

to assess; it may range from that in equilibrium with atmospheric CO_2 up to saturation, depending on many factors, such as the amount of decomposing organic materials in the soil, or the rate of percolation of ground waters. The range of CO_2, then, is from about 10^{-3} to 10^{-1} mols per litre, with the lower figure the expected one in silicate rocks, the higher one in carbonate rocks. Knowledge of total CO_2 and the first and second ionization constants for carbonic acid make it possible to calculate the activity of carbonate ion at any assigned pH. Knowledge of both carbonate and hydroxyl ion permits calculation of the maximum activity of the metal ions in equilibrium with basic carbonates as well as simple carbonates.

The three remaining anions are sulphate, sulphide, and silicate. No data at present are available for the activity products of these metal silicates, but reasonable values for the concentration of sulphate or sulphide ions in the solutions can be obtained. The dissolved sulphur as sulphate or as bivalent sulphur (S^{2-}, HS^-, H_2S) in the reacting ground water is highly variable; it ranges from very low values where rainfall is high and removal of the ground waters is rapid, to several mols per litre under semi-arid conditions, where concentration by evaporation takes place between infrequent rains. In spite of these extremes, an assumption that total soluble sulphur is 0·1 mol per litre represents conditions realized at one time or another; it gives a base from which deviations can be treated. The ratio of sulphide to sulphate depends on the oxidation potential and the pH; distribution of bivalent sulphur among the various bivalent species can be calculated from the known equilibrium constants.

Ratios of the oxidized and reduced states of the metal ions are controlled by the *Eh*; only copper exhibits significant concentrations in more than one valence state.

In summary, the activities of the metal ions are defined if it is assumed that:

1. The ground waters are saturated with CO_2.
2. Total soluble sulphur is 10^{-1} mols per litre.
3. The *Eh* and pH are known.

Again it should be emphasized that this represents a special set of conditions in terms of the assumed concentrations of CO_2 and soluble sulphur. Yet it is a set that does occur, and can serve as a model.

Fields of Lead Mineral Stability

The lead minerals found in the zone of oxidation and secondary enrichment are the sulphide, the sulphate, and the carbonate. The equilibria and assumptions necessary for calculating the maximum activity of lead ion at 25°C are (Latimer, 1938)

$$a_{Pb^{2+}}\, a_{S^{2-}} = K_{PbS} = 10^{-29} \tag{1}$$

$$a_{Pb^{2+}}\, a_{CO_3^{2-}} = K_{PbCO_3} = 10^{-12{\cdot}8} \tag{2}$$

$$a_{Pb^{2+}}\, a_{SO_4^{2-}} = K_{PbSO_4} = 10^{-7{\cdot}75} \tag{3}$$

$$\frac{a_{H^+}\, a_{CO_3^{2-}}}{a_{HCO_3^-}} = K_{HCO_3^-} = 10^{-10{\cdot}5} \tag{4}$$

$$\frac{a_{H^+}\, a_{HCO_3^-}}{a_{H_2CO_3}} = K_{H_2CO_3} = 10^{-6.5} \tag{5}$$

$$\Sigma CO_2 = M_{HCO_3^-} + M_{H_2CO_3} + M_{CO_3^{2-}} = 10^{-1.5} \tag{6}$$

$$\Sigma S = M_{SO_4^{2-}} + M_{S^{2-}} + M_{HS^-} + M_{H_2S} = 10^{-1} \tag{7}$$

$$S^{2-} + 4H_2O = SO_4^{2-} + 8H^+ + 8e; \quad E^0 = -0{\cdot}14 \tag{8}$$

$$\frac{a_{H^+} a_{S^{2-}}}{a_{HS^-}} = K_{HS^-} = 10^{-15} \tag{9}$$

$$\frac{a_{H^+}\, a_{HS^-}}{a_{H_2S}} = K_{H_2S} = 10^{-7} \tag{10}$$

In the following calculations it will be assumed the $M = a_i$, ignoring the activity coefficient. The error resulting is not large for solutions of low ionic strength (μ), but may be serious at values of μ much exceeding 0·1.

SULPHATE-SULPHIDE RATIO AND ACTIVITIES

The sulphide-sulphate ratios can be obtained from the oxidation equation (8). At 25°C:

$$Eh = -E^0 + \frac{RT}{nF} \ln \frac{a_{SO_4^{2-}} (a_{H^+})^8}{a_{S^{2-}}}$$

For an arbitrary pair of values ($Eh = 0{\cdot}4$; $p\mathrm{H} = 1$) representing the acid oxidizing conditions expected at the ground surface:

$$0{\cdot}4 = 0{\cdot}14 + 0{\cdot}0075 \log \frac{a_{SO_4^{2-}} (10^{-1})^8}{a_{S^{2-}}}$$

$$\frac{a_{SO_4^{2-}}}{a_{S^{2-}}} = 10^{42{\cdot}6}$$

From equation No. 7:

$$M_{SO_4^{2-}} + M_{S^{2-}} + M_{HS^-} + M_{H_2S} = 10^{-1}$$

Also, at this pH, from equations No. 9 and No. 10:

$$\frac{a_{S^{2-}}}{a_{HS^-}} = 10^{-14}; \quad \frac{a_{S^{2-}}}{a_{H_2S}} = 10^{-20}$$

Substituting from the ratios:

$$10^{42{\cdot}6}\, M_{S^{2-}} + M_{S^{2-}} + 10^{14} M_{S^{2-}} + 10^{20} M_{S^{2-}} = 10^{-1}$$

$$M_{SO_4^{2-}} = a_{SO_4^{2-}} \cong 10^{-1}$$

$$M_{H_2S} = a_{H_2S} = 10^{-23{\cdot}6}$$

$$M_{HS^-} = a_{HS^-} = 10^{-29{\cdot}6}$$

$$M_{S^{2-}} = a_{S^{2-}} = 10^{-43{\cdot}6}$$

Carbonate Ion Activity

The activity of carbonate ion is independent of Eh. At pH 1, from equations (4) and (5):

$$\frac{a_{CO_3^{2-}}}{a_{HCO_3^-}} = 10^{-9.5}; \frac{a_{HCO_3^-}}{a_{H_2CO_3}} = 10^{-5.5}$$

Substituting from these ratios in equation (6):

$$M_{HCO_3^-} + 10^{-9.5} M_{HCO_3^-} + 10^{5.5} M_{HCO_3^-} = 10^{-1.5}$$

$$M_{HCO_3^-} = \frac{10^{-1.5}}{10^{5.5}} = 10^{-7}$$

$$M_{CO_3^{2-}} = a_{CO_3^{2-}} = 10^{-7} \times 10^{-9.5} = 10^{-16.5}$$

Determination of a Stable (Least Soluble) Mineral

Under the conditions chosen, calculations yielded $a_{SO_4^{2-}} = 10^{-1}$, $a_{S^{2-}} = 10^{-43.6}$; $a_{CO_3^{2-}} = 10^{-16.5}$. From equations (1), (2), and (3):

$$a_{Pb^{2+}} = \frac{10^{-7.75}}{a_{SO_4^{2-}}} = 10^{-6.75} \quad (1)$$

$$a_{Pb^{2+}} = \frac{10^{-12.8}}{a_{CO_3^{2-}}} = 10^{4.3} \quad (2)$$

$$a_{Pb^{2+}} = \frac{10^{-29}}{a_{S^{2-}}} = 10^{14.6} \quad (3)$$

The activity of lead ion in equilibrium with sulphate is much less than that with the other anions; presumably lead sulphate (anglesite) is the stable (least soluble) mineral.

It is not necessary to calculate an infinite number of points to determine the field of stability of the various solid phases, because the boundaries between fields are conditions in which both solids are in equilibrium with their ionic constituents. For example, at a boundary between $PbCO_3$ and $PbSO_4$ the following relations hold:

$$(Pb^{2+})\,(SO_4^{2-}) = K_{PbSO_4}$$

$$(Pb^{2+})\,(CO_3^{2-}) = K_{PbCO_3}$$

For a given pH and Eh, SO_4^{2-} concentration can be calculated, as has been shown. This determines the Pb^{2+} in equilibrium with the solid lead sulphate. In turn, this value of Pb^{2+} can be used to define the CO_3^{2-} in equilibrium with $PbCO_3$. From this equilibrium amount of CO_3^{2-} ion the pH can be calculated from the dissociation constants for the carbon dioxide species.

A series of such calculations has been used to construct Fig. 1.

Discussion

The diagram shows the fields of stability of the three lead minerals, as well as contours of the activity of lead ion. These activities are maximum values; on the other hand they are minima for the stoichiometric solubility of lead. The ionic strength effect on the activity coefficients has been ignored; the effect might

cause a tenfold increase in lead solubility. Also, any lead complexes would increase total lead in solution. No important complexes with low dissociation constants are known for such a system, but there is always the possibility that they exist.

The actual behaviour of lead sulphide in the zone of oxidation indicates that the calculated activity of lead ion is the same order of magnitude as the solubility

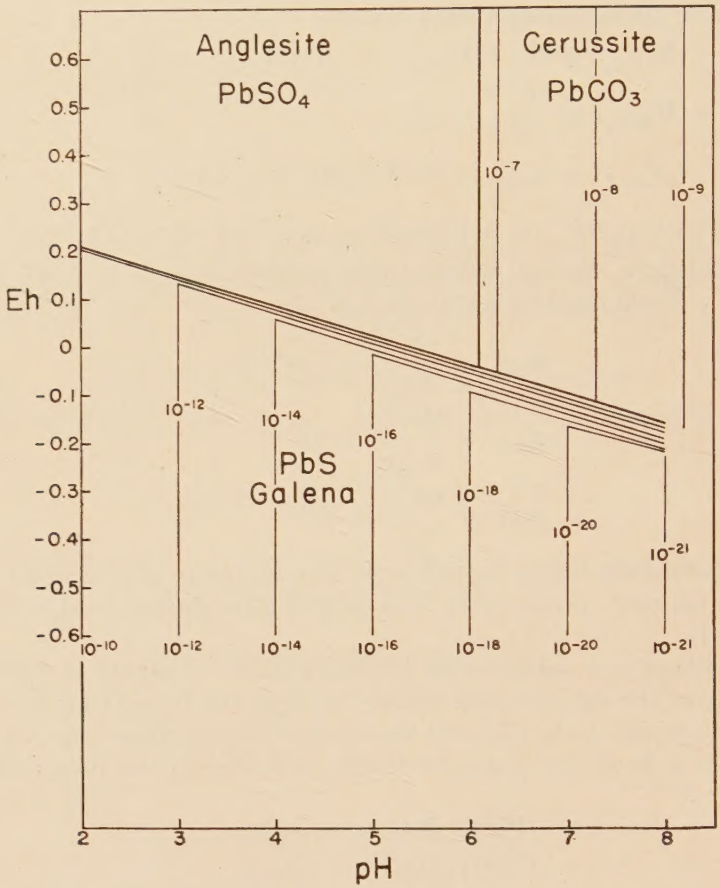

Fig. 1. Fields of stability of some lead compounds as functions of pH and Eh. Contours are for activity of Pb^{2+}.
($\Sigma CO_2 = 0{\cdot}03$ M; $\Sigma S = 0{\cdot}1$ M; $t = 25°C$)

in the natural system. The maximum calculated activity for the assumed condition is of the order 10^{-7}; from this it would be predicted that lead could not be transported in ground waters. It is clear from the field relations that it is not. The common occurrence of mineral masses with a lead sulphide core, surrounded by a lead sulphate shell, in turn surrounded by a lead carbonate shell, has a reasonable explanation on the basis of the diagram. At the site of oxidation an acid solution is formed, and the sulphide is converted to sulphate. As the hydrogen ions move outward from the sulphide-sulphate reaction zone they are neutralized by calcium

carbonate, and an outer zone of lead carbonate is built up by slow solution of the lead sulphate and precipitation of the carbonate.

The effect of a different quantity of soluble sulphur can be assessed here. If the concentration were 10^{-3} mols per litre instead of 10^{-1}, the activity of lead ion in equilibrium with the sulphate would be increased to about 10^{-5} mols per litre; the anglesite-cerussite boundary on the diagrams would be moved from pH 6 to pH 5·5. The boundary between anglesite and galena, and that between cerussite and galena, would be changed very little, because its position is extremely sensitive to small changes in *Eh*, and insensitive to total sulphur. The rapidly changing SO_4^{2-}/S^{2-} ratio completely overshadows a 100-fold change in total soluble sulphur. Even at this low concentration of SO_4^{2-}, the solubility of all three solid phases is very low—but a few parts per million.

When galena occurs in silicate rocks, anglesite is the common oxidation product. The absence of lead carbonate is to be expected unless the matrix is of some material capable of rapid neutralization of the acid produced during oxidation. If lead moves at all in solution, it should do so when it occurs in non-carbonate rocks in areas of high rainfall and good drainage.

Fields of Copper Mineral Stability

Of the many copper minerals found in the zone of oxidation and secondary enrichment, only five are treated herein. They are tenorite (CuO), cuprite (Cu_2O), native copper (Cu), covellite (CuS), and chalcocite (Cu_2S). Their fields of stability are shown in Fig. 2. The equilibria and assumptions necessary for calculating the maximum activity of copper ($a_{Cu^{2+}} + a_{Cu^+}$) are (Latimer, 1938):

$$a_{Cu^{2+}} a^2_{OH^-} = K_{Cu(OH)_2} = 10^{-19{\cdot}25} \tag{4}$$

$$Cu(OH)_2 = CuO + H_2O$$

$$a_{Cu^+} a_{OH^-} = K_{Cu(OH)} = 10^{-14{\cdot}9} \tag{5}$$

$$2CuOH = Cu_2O + H_2O$$

$$Eh = 0{\cdot}167 + 0{\cdot}06 \log \left[\frac{a_{Cu^{2+}}}{a_{Cu^+}}\right] \tag{6}$$

$$Eh = 0{\cdot}522 + 0{\cdot}06 \log \left[\frac{a_{Cu^+}}{a_{Cu^0}}\right] \tag{7}$$

$$Eh = 0{\cdot}14 + 0{\cdot}0075 \log \left[\frac{a_{SO_4^{2-}} a^8_{H^+}}{a_{S^{2-}}}\right] \tag{8}$$

$$\frac{a_{H^+} a_{S^{2-}}}{a_{HS^-}} = K_{HS^-} = 10^{-15} \tag{9}$$

$$\frac{a_{H^+} a_{HS^-}}{a_{H_2S}} = K_{H_2S} = 10^{-7} \tag{10}$$

$$a_{Cu^{2+}} a_{S^{2-}} = K_{CuS} = 10^{-37{\cdot}4} \tag{16}$$

$$a^2_{Cu^+} a_{S^{2-}} = K_{Cu_2S} = 10^{-49{\cdot}6} \tag{17}$$

As before, the calculation of a point on the diagram may suffice to show the method of construction. At the arbitrary pair of values $Eh = 0{\cdot}4$, $p\mathrm{H} = 4$ ($a_{\mathrm{OH^-}} = 10^{-10}$):

$$a_{\mathrm{Cu^{2+}}} = \frac{10^{-19{\cdot}25}}{(10^{-10})^2} = 10^{0{\cdot}75} = \text{maximum activity of } \mathrm{Cu^{2+}} \text{ in equilibrium with cupric hydroxide.} \tag{11}$$

$$a_{\mathrm{Cu^{+}}} = \frac{10^{-14{\cdot}9}}{10^{-10}} = 10^{-4{\cdot}9} = \text{maximum activity of cuprous ion in equilibrium with cuprous hydroxide.} \tag{12}$$

$$0{\cdot}4 = 0{\cdot}167 + 0{\cdot}06 \log \frac{a_{\mathrm{Cu^{2+}}}}{a_{\mathrm{Cu^{+}}}} \tag{13}$$

$\dfrac{a_{\mathrm{Cu^{2+}}}}{a_{\mathrm{Cu^{+}}}} = 10^{3{\cdot}9}$ = equilibrium ratio of cupric and cuprous ions.

$$0{\cdot}4 = 0{\cdot}522 + 0{\cdot}06 \log \frac{a_{\mathrm{Cu^{+}}}}{a_{\mathrm{Cu^{0}}}} \tag{14}$$

$\dfrac{a_{\mathrm{Cu^{+}}}}{a_{\mathrm{Cu^{0}}}} = 10^{-2{\cdot}03}$; or maximum activity of $\mathrm{Cu^{+}}$ in equilibrium with native copper.

$$0{\cdot}4 = 0{\cdot}14 + 0{\cdot}0075 \log \frac{a_{\mathrm{SO_4^{2-}}}\, a^8_{\mathrm{H^{+}}}}{a_{\mathrm{S^{2-}}}} \tag{15}$$

$\dfrac{a_{\mathrm{SO_4^{2-}}}}{a_{\mathrm{S^{2-}}}} = 10^{66{\cdot}8}$; thus, equilibrium amount of sulphide ion present is $10^{-67{\cdot}8}$, if total sulphur is 10^{-1}. (At such a high $\dfrac{\mathrm{SO_4^{2-}}}{\mathrm{S^{2-}}}$ ratio, the sulphur bound up in $\mathrm{HS^-}$ and $\mathrm{H_2S}$ [Equations (9) and (10)] can be ignored.)

$$a_{\mathrm{Cu^{2+}}} = \frac{10^{-37{\cdot}4}}{10^{-67{\cdot}8}} = 10^{30{\cdot}4} = \text{maximum activity of cupric ion in equilibrium with cupric sulphide.} \tag{16}$$

$$a_{\mathrm{Cu^{+}}} = \frac{10^{-49{\cdot}6}}{10^{-67{\cdot}8}} = 10^{18{\cdot}2} = \text{maximum activity of cuprous ion in equilibrium with cuprous sulphide.} \tag{17}$$

From these relations, the total cuprous plus cupric ion is limited by the solubility of cuprous hydroxide and the cupric-cuprous ratio. The maximum activity of cuprous ion is $10^{-4{\cdot}9}$ (Equation (12)). Therefore the activity of cupric ion from equation (13) is:

$$\frac{a_{\mathrm{Cu^{2+}}}}{10^{-4{\cdot}9}} = 10^{3{\cdot}9}; \quad a_{\mathrm{Cu^{2+}}} = 10^{-1}$$

This value is less than the activity of cupric ion in equilibrium with any of the solids. Under the stated conditions, then, cuprous hydroxide is the stable solid, and total copper is defined by the cuprous ion in equilibrium with this compound, plus the cupric ion in equilibrium with cuprous ion at the stated oxidation potential.

$$\text{Total copper} = a_{\mathrm{Cu^{+}}} + a_{\mathrm{Cu^{2+}}} = 10^{-4{\cdot}9} + 10^{-1} \cong 10^{-1}$$

Discussion

In the CuO field of Fig. 2, solubility is due almost entirely to the cupric ion, and the control, as shown by the contours parallel to the *Eh* axis, is a_{OH^-}.

In the Cu_2O field the solubility still can be attributed to the contribution of the

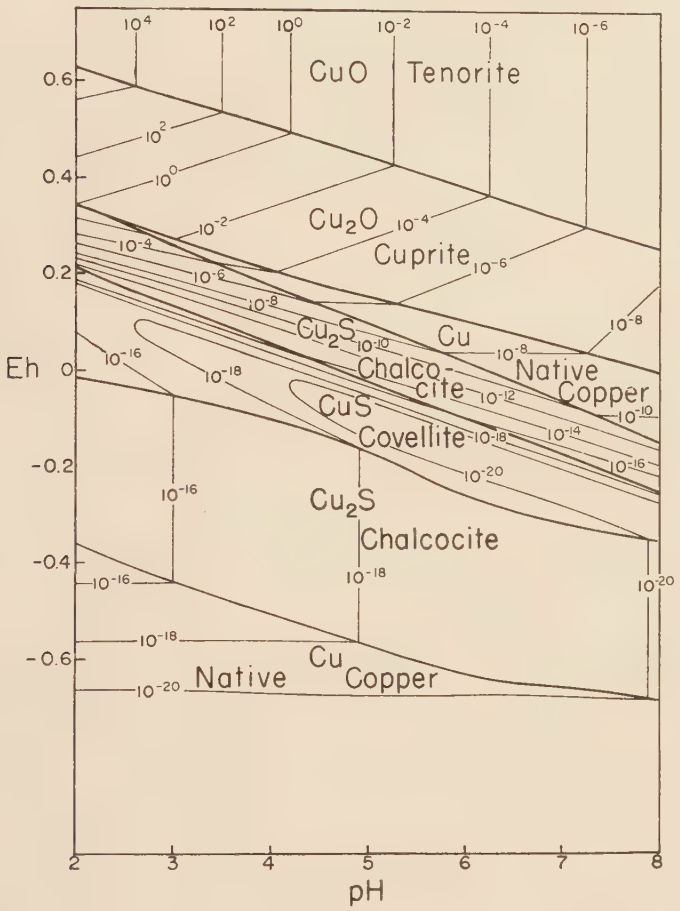

Fig. 2. Fields of stability of some copper compounds as functions of pH and *Eh*. Contours are for activity Cu^{2+} + activity Cu^+.
($\Sigma S = 0{\cdot}1$ M; $t = 25°C$)

cupric ion, but the cupric ion activity is determined by the amount in equilibrium with the cuprous ion, which is in turn in equilibrium with the solid cuprous hydroxide. Thus a_{Cu^+} depends only on pH, whereas $a_{Cu^{2+}}$ depends on both pH and *Eh*, and the contours show this dependence by their slope.

In the native copper field, the contribution of cupric ion is small, so that the contours show the *Eh* dependence and pH independence of the cuprous ion in equilibrium with native copper.

As the oxidation potential becomes lower, small amounts of sulphide ion are

in equilibrium with sulphate and the lower boundary of the native copper field is reached when the sulphide becomes sufficient to precipitate Cu_2S.

The Cu_2S gives way to CuS as the sulphide ion increases; Cu_2S again becomes stable when the potentials are sufficiently low to give an extremely small cupric-cuprous ratio.

At very low *Eh* values the cuprous ion concentration in equilibrium with native copper becomes so low that even the very difficultly soluble sulphide cannot form, and a second field of stability of native copper appears. It is unlikely that native copper actually forms in nature under these conditions—at such low potentials water would decompose to yield hydrogen, and it appears doubtful that such conditions are attained. If so, formation of native copper takes place in the intermediate zone only under conditions sufficiently reducing to form native copper in preference to the oxides, but not sufficient to stabilize sulphide ion.

The diagram fits field relations well. Cuprite and native copper are common associates in the "zone of oxidation," and chalcocite is the most common sulphide developed at and below the level of saturation with ground water, where potentials are lower. Minor amounts of covellite also occur. Solubility under the acid-oxidizing conditions at the ground surface is large, as attested by the active migration of copper; the diagram shows high values. The copper content of natural streams, even in the areas of copper mining, is extremely low. Such streams have *p*H values of 7·5 to 8, and probably have *Eh* values of the order of 0·3 or 0·4. The absence of appreciable copper in solution under such conditions could have been predicted from the diagram.

The diagram can be used, in conjunction with our knowledge of natural mineral associations, to determine rough values for the solubility product constants of compounds for which data are not available in the chemical literature. For example, the mineral malachite ($Cu_2(OH)_2CO_3$) is a common associate of cuprite in limestones. The minerals occur intergrown so that they probably coprecipitated. In limestones the *p*H of ground waters is of the order of magnitude of 7·5 to 8, and it is safe to assume that acid oxidation of the sulphides produces a solution saturated with CO_2. Under these conditions the carbonate ion activity is approximately 10^{-5}. Substituting these values in the equation for activity product:

$$(a_{Cu^{2+}})^2(a_{CO_3^{2-}})(a_{OH^-})^2 = K_{Cu_2CO_3(OH)_2}$$
$$10^{-14} \times 10^{-5} \times 10^{-13} = 10^{-32}$$

The value is useful, even though it represents only an order of magnitude.

Fields of Zinc Mineral Stability

Among the zinc minerals found in the zone of oxidation and secondary enrichment are the sulphide, carbonate, basic carbonate, oxide, and the (basic?) silicate. Of these, activity products are only available for the carbonate, oxide (hydroxide), and sulphide. The equilibria and assumptions necessary for calculating the maximum activity of zinc ion at 25°C are (Latimer, 1938):

$$a_{Zn^{2+}}a_{CO_3^{2-}} = K_{ZnCO_3} = 10^{-10\cdot2} \quad (18)$$

$$a_{Zn^{2+}}a_{S^{2-}} = K_{ZnS} = 10^{-23\cdot3} \quad (19)$$

$$a_{Zn^{2+}} a^2_{OH^-} = K_{Zn(OH)_2} = 10^{-16.3} \tag{20}$$

$$\frac{a_{ZnO_2^{2-}}}{a_{Zn^{2+}} a^2_{OH^-}} = K_{ZnO_2^{2-}} = 10^{-15.5} \tag{21}$$

$$\frac{a_{ZnOH^+} a_{H^+}}{a_{Zn^{2+}}} = K_{ZnOH^+} = 10^{-9.6} \tag{22}$$

$$Eh = 0.14 + 0.0075 \log \frac{a_{SO_4^{2-}} a^8_{H^+}}{a_{S^{2-}}} \tag{15}$$

Zinc differs from lead and copper in that there are important complexes expected in the natural system. For zinc the effect of the complexes formed in alkaline

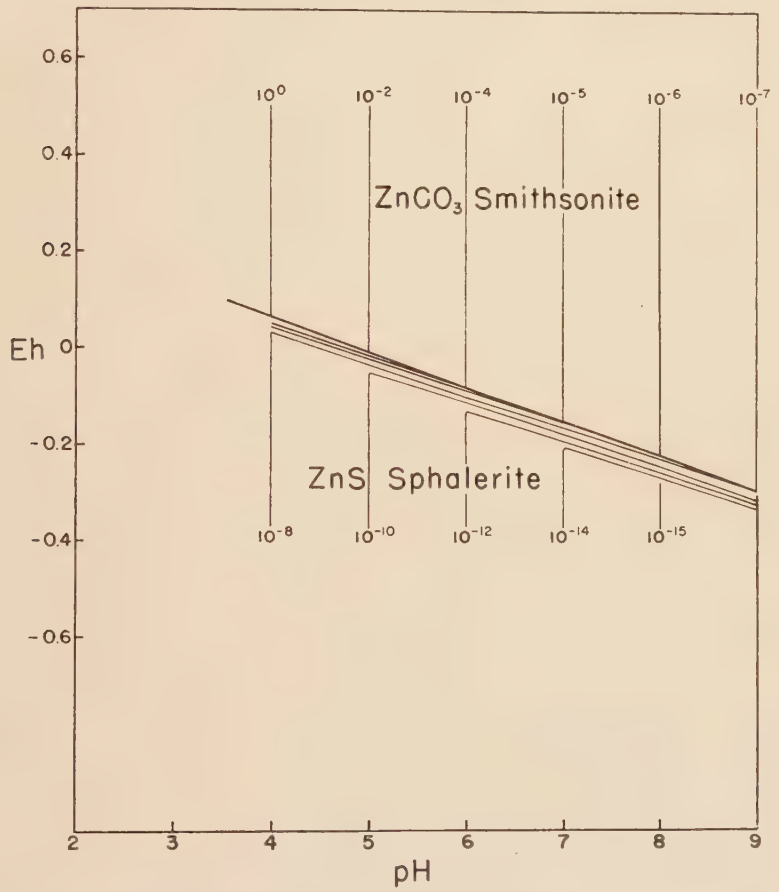

Fig. 3. Fields of stability of some zinc compounds as functions of pH and Eh. Contours are for activity Zn^{2+}.
($\Sigma CO_2 = 0.03$ M; $\Sigma S = 0.1$ M; $t = 25°C$)

solution can be included in a separate "solubility" diagram that serves to show the important differences in solubility occasioned by the presence of complexes with low dissociation constants.

Calculation of stability fields for zinc is similar to that for lead and copper, and presents no new problems, so that no sample calculation is presented.

Fig. 3 shows the zinc ion activity diagram, and Fig. 4 the zinc "solubility" diagram. Fig. 4 is not, of course, a true solubility diagram, but one in which the activity of the important complex (ZnO_2^{2-}) is added to the activity of the zinc ion.

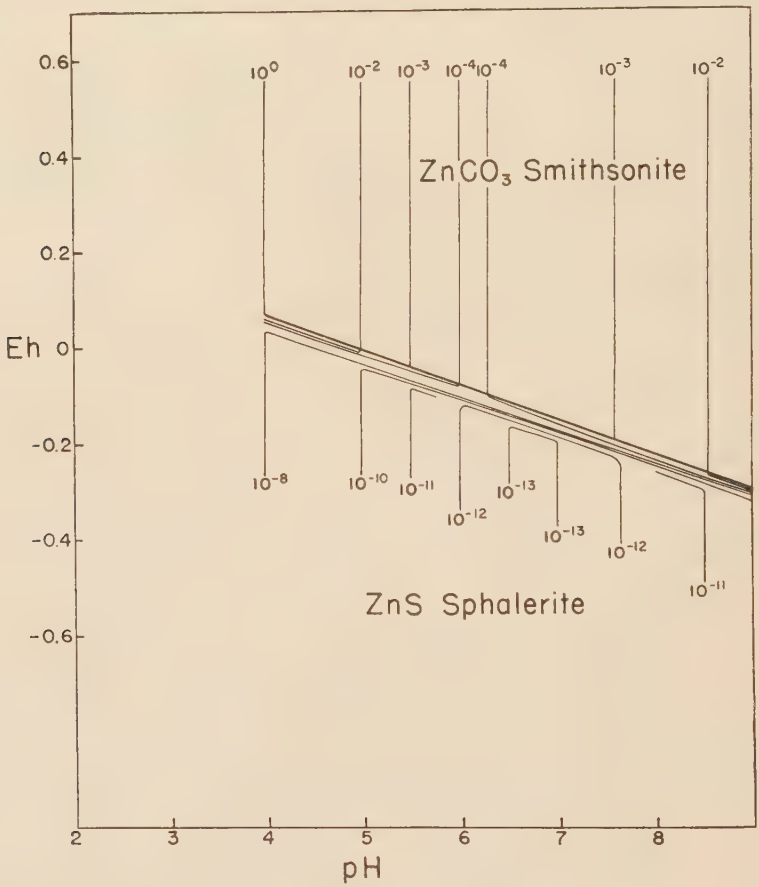

Fig. 4. Fields of stability of some zinc compounds as functions of pH and Eh. Contours are for activity of Zn^{2+} + activity ZnO_2^{2-}.
($\Sigma CO_2 = 0{\cdot}03$ M; $\Sigma S = 0{\cdot}1$ M; $t = 25°C$)

Discussion

The zinc ion activity (Fig. 3) is similar to that for lead. The major differences are the absence of an insoluble sulphate in the zinc system, and the considerably greater activity of zinc in equilibrium with the sulphide. Only the carbonate and the sulphide appear on the diagram; in systems saturated with CO_2 the carbonate is less soluble at all pH values than the hydroxide. The presence of the hydroxide in zinc deposits presumably represents a low CO_2 content of the natural waters.

In Fig. 4 the effect of the complex ZnO_2^{2-} is shown. The "solubility" reversal at approximately pH = 7 is present in both carbonate and sulphide stability fields.

It is noteworthy that even when known complexes are considered the calculated solubility of zinc in slightly acid or slightly alkaline reducing solutions is still very low, and zinc would not be expected to migrate if equilibrium is attained. This is contrary to the observation that zinc is not found as a secondary sulphide in the zone of secondary enrichment at the water table. The active migration of zinc in the zone of oxidation is readily understood on the basis of the solubility minimum of the carbonate of about 10^{-4} mols per litre. This figure would not be affected, of course, by assumption as to total soluble sulphur in the system.

Overall Relations

In Fig. 5 the fields of stability of all the minerals discussed have been placed on a single diagram. The presumed reactions that take place in the earth can be followed by reference to the capital letters on the diagram. The primary sulphides (PbS, ZnS, $CuFeS_2$) exist, before exposure at the surface of the earth, in an environment indicated at C. The sulphides are stable, and are very slightly soluble, so that they continue to exist indefinitely without corrosion or other reactions. When the deposit is exposed, oxidation of the sulphides takes place, with the development of an acid oxidizing environment (B). The lead sulphide becomes coated with insoluble sulphate, whereas the copper and zinc migrate. With progressive neutralization and removal of oxygen from the solutions, the descending ground waters follow a path from B to C. This is a path of decrease in solubility. Any small amount of lead moving is precipitated as the sulphate or carbonate, copper is progressively precipitated as CuO, Cu_2O, and as Cu. The relative amounts precipitated probably depend on the rate at which the solutions pass through the various environments, which is a function of the nature of the rock, the amount of rainfall, and so forth. Any copper remaining in solution is precipitated essentially completely as chalcocite when the ground water level is reached, and environment C is entered.

The absence of secondary PbS at C is explainable on the basis of the very low solubility of lead compounds in all environments, but the absence of secondary ZnS is a more difficult problem. There is little question that most of the zinc disappears from these deposits. Its migration in the carbonate stability field is expected, but its absence near the ground water table is not.

Several possibilities can be suggested. First, there may be an aspect of the chemistry that has been overlooked, such as the formation of a zinc complex in addition to ZnO_2^{2-}. This does not appear reasonable, for primary zinc sulphide shows no tendency to migrate, indicating that the calculated low solubility in environment C is reasonable. Second, the sulphide may supersaturate, or move colloidally. The long times involved would seem to rule out supersaturation, and the difficulty of transporting colloids through rock pores and fractures makes such colloidal transportation unlikely. The most likely explanation is based on the extremely slow rate of reduction of sulphate ion to sulphide in inorganic systems. If sulphate is not reduced to sulphide in environment C, then precipitation of secondary sulphides must depend on production of sulphide ions from primary sulphides. Zone C would then appear as a zone of sulphide stability rather than sulphate reduction. If so, only those sulphides would reprecipitate that could

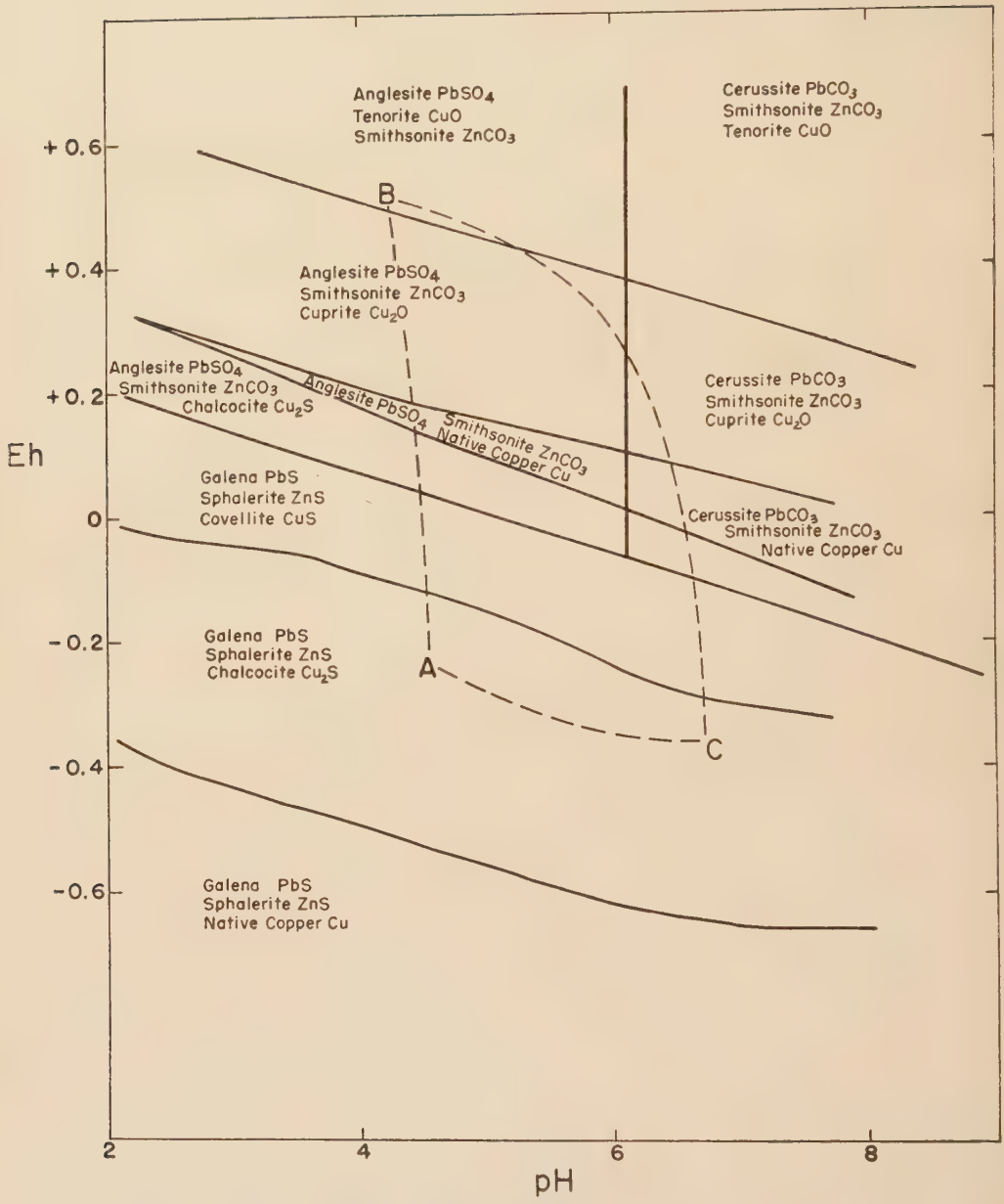

Fig. 5. Composite diagram of fields of stability of copper, lead, and zinc compounds.

obtain sulphide ion from pre-existing metal sulphides; in other words, the least soluble species.

Copper would be expected to reprecipitate by removing sulphide ion from primary zinc or lead sulphide, and perhaps even from primary copper-iron sulphide, whereas zinc, the most soluble sulphide, would continue to move in solution.

Viewed in another way, the reason for the absence of zinc as a secondary sulphide at the ground water table is a deficiency of sulphide ions, caused by the slow rate of reduction of sulphate. Under these circumstances, where the amount of sulphide ions is not sufficient to satisfy all the metals moving in solution, only the least soluble will form.

The path B–C shown presumes that the sulphides are in a limestone matrix, and solutions should be neutralized rapidly; alternate path B–A–C is suggested for the case in which the matrix is a common igneous rock. In limestones a great deal of the copper would be expected as oxides and basic carbonates in the zone of oxidation; in igneous rock the concentration of copper would be in the secondary sulphide zone.

The values chosen for environments B and C are not from direct measurements of Eh and pH in deposits of the kind discussed, but are analogies drawn from measurements in normal soils. The need for direct measurements is obvious.

The small variation in the position of the boundary below which sulphides are stable makes it possible to delimit with fair accuracy the "zone of oxidation" from the "zone of secondary enrichment." A straight line from Eh 0·2 at pH 2, to Eh −0·2 at $p\text{H} = 10$ separates very well the environments classified as "oxidizing" and "reducing" by geologists. These terms have been generally used to denote the zone above the water table as opposed to the zone below. At the same time, there was a tendency to use the mineralogy, much as it has been used here, to define these zones. Considerable ambiguity arose, however, because as the terms were used, there was a strong implication that in the oxidizing zone essentially all elements were in higher valence states, and there was no definite answer to the question "reducing (or oxidizing) relative to what species?" As proposed here, the basis is the stability or instability of the metal sulphides, and the boundary between the zones is defined relative to the standard potential of the hydrogen electrode. It is perhaps worth noting, to illustrate the confusion that existed in the author's mind, at least, that even under the most oxidizing conditions present in nature, it is not likely that the Fe^{3+}/Fe^{2+} ratio in solution is greater than unity.

Summary and Conclusion

Eh–pH diagrams have been prepared for minerals formed at low and constant temperature and pressure. These theoretical diagrams reproduce the major gross mineral association relations observed in the field. The implication is strong that natural systems are surprisingly close to equilibrium systems except for the persistence of sulphate ion under conditions theoretically sufficiently reducing to change it to sulphide ion. Also, the maximum activities calculated apparently are approximations of the order of magnitude of actual solubilities under natural conditions.

These diagrams promise to be useful in a number of ways. They provide a

convenient boundary between the "zone of oxidation" and "zone of secondary enrichment." Over and above the specific problems of the oxidation of sulphides, they provide a set of calculated equilibrium relationships among various mineral species. Although the diagrams are based upon several compositional approximations, the gross relationships provide a framework for comparison with natural deposits, and for experimental investigation. From observed mineral relations obvious errors in the diagrams may appear. Conversely, attention may be directed by the diagrams to anomalous mineral associations.

Most important, perhaps, is that study of the diagrams is helpful in suggesting new lines of approach to geologic problems, or gives support to a particular solution of a problem that had several possible explanations.

For example, this study suggests relationships in rather diverse problems. It emphasizes the difficulty of reducing sulphate to sulphide in inorganic systems, and again stresses the role of organisms in the production of pyrite and other primary sulphides in sediments.

If it is observed that lead is "travelling" in a given deposit, unusual complexing agents, such as organic materials, should be suspected. If the concentration of lead in ground waters is far less than that predicted, adsorption processes may be at work.

If, as is suggested by the diagrams, equilibrium is approached in the ionic solutions considered, what happens to colloidal materials moving downward? Do they respond to the environment?

These questions could be multiplied, but they are raised to make a point: These diagrams are not accurate representations of natural systems; and they undoubtedly are highly variable in their approach to that ideal. Yet because they represent a quantitative estimate based on the available data, they should be helpful tools, if used within their limitations.

The manuscript has been read by T. S. Lovering, Harold James, and Walter White of the U.S. Geological Survey, Richard Gault of Lehigh University, John Ridge of the Pennyslvania State College, and Brian Mason of Indiana University. I have benefited greatly from their many comments, suggestions, and criticisms. In this final version I have attempted to make the changes they have suggested, and hope that the results are satisfactory to them.

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Coloured natural rocksalts: a study of their helium contents, colours and impurities

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ABSTRACT

A study has been made of the quantities of helium occluded in natural, coloured rocksalts and a correlation found between the colour of the salts and the helium content. All the helium in the salts cannot have arisen from radioactive disintegration of uranium and thorium in 10^8 years, for the concentrations of these elements have now been measured and found to be inadequate. The uranium was estimated fluorimetrically and the thorium by α-particle scintillation counting. Hahn's hypothesis for the origin of the helium is accepted and an alternative source for some of the helium proposed. Loss of helium from the salts by diffusion has been observed. The absorption spectra of the yellow, blue and violet salts have been measured and the nature of the colour centres is considered. A spectrographic analysis has been made of the salts, and the mechanism of impurity sensitisation to colour production by radiation is discussed.

1. Introduction

Helium content and age of the rocksalts

The form and composition of the Stassfurt salt deposits suggest a marine origin (van't Hoff, 1901) for the initial layers containing the primary rocksalt and a more complex origin for the later gypsum, anhydrite and secondary rocksalts. The calcium content of these secondary deposits is far in excess of that to be expected from the simple evaporation of sea water (Mellor, 1922) and some at least of the secondary deposits seem to have arisen from inland lakes fed by fresh water.

Since the rocksalts contain helium (the primary about 10^{-8} cc/g and the secondary 10^{-7} cc/g) and uranium and radium in radioactive equilibrium (Kemeny, 1941; Karlik and Kropff-Duschek, 1949, 1950; Paneth and Peters, 1928; Strutt, 1908; Born, 1934; Valentiner, 1912), one can make premature calculations of the ages of the deposits. Since thorium concentrations were not available and comparisons were made between helium in some samples and uranium in others, the results are of doubtful validity. The ages obtained are of the order of 10^{10} years, and in the view of the well established geological age of the deposits of 10^8 to 10^7 years (Smits and Gentner, 1950; Kemeny, 1941) sources have been suggested for the large amounts of helium in the salts.

We have considered three sources of helium: 1. Hahn and H. J. Born's suggested source, 2. the thorium contained in a salt sample, 3. occlusion of helium during growth of the crystals.

1. Hahn (1934) has suggested that the inclusion of a lead isotope, radium D, in the salts might give rise to the helium. Born (1934) has calculated, however, that the radium D in equilibrium with the radium in sea water (10^{-11} g/litre) is not sufficient to give rise to the helium in the secondary salts. He therefore postulated that these salts have been crystallised from "natural deep waters" rich in radium and radium D. Hahn and Born (1935) have examined the natural waters

from various localities in Germany and found 10^{-15} to 5×10^{-9} g Ra/litre. The radium D in equilibrium with this radium would be adequate to account for the helium in the salts.

Support for this hypothesis can be found if the lead contents of natural rocksalts are examined. The concentrations are high enough to include sufficient lead from radioactive decay to account for the helium. Furthermore the helium content of the secondary salts is, in general, higher than that of the primary salt of marine origin (Born, 1934), although a few exceptions to this have been observed (Karlik and Kropf-Duschek, 1950). Hahn and Born have noted that a high calcium content in natural waters accompanies a high radium content. Since the secondary deposits are rich in calcium it seems reasonable to suggest that they have crystallised from water rich also in radium.

2. Previously the estimation of thorium in trace amounts by counting was difficult owing to high background counting rates, but we have had the thorium content of a sample measured using a scintillation counting technique. The advantage of this type of counter was its low natural background counting rate of one per hour. Approximately 5×10^{-6} g thorium would be required per gram of salt to produce the helium it contains in 10^8 years.

3. Since it is likely that both the primary and secondary rocksalts would crystallise from water containing helium either from air saturation or from radioactivity in the water, it seemed advisable to examine a specimen of salt grown in the laboratory in a solution saturated with air.

Colour of natural rocksalts

Certain secondary rocksalts are believed to be coloured not by impurity, but by the influence of radiations from occluded radioactive elements, ^{40}K, U, Th, Po, etc. The absorption spectra of these coloured salts have been examined by Wieninger (1953) who has classified the colours and the type of colour centres, etc. as follows:

(a) yellow	*F*-centres.
(b) violet	*F*, *R*11, *M*-centres.
(c) blue	*R*1-centres, colloidal metal, impurities.
(d) blue-violet	*R*11-centres, colloidal metal.

Siedentopf (1905) has identified colloidal metal in the natural blue rocksalts.

There are certain differences between these salts, coloured by irradiation, and additively coloured salts. Salts coloured by irradiation are stoichiometric and have a neutral reaction in solution (Phipps and Brode, 1926) but opinion is divided about the reactions of the natural blue salt (Mellor, 1922, p. 530). The nature of the *V*-band is such that it is unlikely to be present in additively coloured salts: this band should however appear in salts coloured by irradiation (Alexander and Schneider, 1949) but it has not been identified so far in naturally coloured rocksalts. Differences also arise in the thermal bleaching of the colours in the two types of crystals. On raising the temperature of an irradiation coloured crystal

to 250°C the colour can be removed completely and it does not reappear on cooling. Additively coloured crystals, however, retain their colours on heating and cooling (Adler, 1949; Phipps and Brode, 1926).

The yellow coloration arises from F-centres and this is regarded as the primary coloration. The initial products of combination of F-centres are the R- and M-centres. Coagulation of colour centres in an irradiated crystal has been observed in the laboratory as a result of heat treatment, pressure, irradiation with white light, or light lying in the F-band, but not to the extent of formation of colloidal metal. To account for the coagulation of colour centres to produce colloidal metal, Przibram has assumed that a process of sensitisation of the salts occurs through the occlusion of impurity as is the case in the silver halides containing silver sulphide (Mitchell, 1949). Impurity gives rise to an absorption maximum only in the blue salt, and Wieninger (1951) supports the view of Przibram in that the former attributes the formation of colloids specifically to sulphur. The depth of colour of irradiation origin, attained in the fluorites, has already been related to the sulphur content of the specimen (Steinmetz, 1923; 1925).

Lead is another impurity which might lead to sensitisation towards colour and colloid formation and Born (1934) has examined this possibility in the irradiation of a series of salts containing lead. As lead content increased in the crystals the stability of the yellow colour decreased and the yellow colour was replaced by blue. Other investigations have indicated an optimum concentration for sensitisation by divalent cations (Jahoda, 1926; Smakula, 1929).

Since R- and M-band maxima have been observed in some of the coloured samples it seems reasonable to suggest that in geological time the influence of pressure, temperature, and impurity has caused F-centres to coagulate to form R- and M-centres and colloids. The suggestion that the impurities could aid coloration is supported by the appearance of the coloured salts. Whilst some samples of our salts appear to be uniformly coloured, close examination shows that in others, the colours occur in striae. This striation is typical of the way in which colours occur in salts which are coloured only by the inclusion of substances like ferric oxide. Inclusion of sensitising impurities at grain boundaries should result, therefore, in the appearance of striae in the irradiation coloured salts.

Przibram (1951) supports the belief that the colour has irradiation as basis and calculates that the energy available for this purpose from the radioactive sources present in the crystal is quite adequate, provided one assumes the same end effect from a weak source acting over a considerable time as from a strong source over a short period of time.

The sources of energy he considers are:

1. The uranium-radium content.
2. Polonium α-particles (calculated from the helium content).
3. K^{40} content.

The energy from each source is considered separately and is found to be sufficient in each case so that the total, when all are considered as acting together, is eminently sufficient. Adler *et al* (1952) find the ^{40}K activity sufficient to colour only the yellow variety and not the blue.

In spite of this strong argument in favour of an irradiation colour several questions are still not answered satisfactorily. Why, for instance, are not all rocksalts coloured? In the secondary layer at least, the available sources of energy appear to be identical in both the coloured and uncoloured salts.

Przibram assumes some particular form of sensitisation in the coloured variety due to plastic deformation or impurity. Of the two, impurity seems the more likely since this could deposit with the salt in the earlier crystallisation and not in the later, whereas plastic deformation would probably apply to the layer as a whole. If the sensitisation is due to impurity then chemical analysis should reveal a significant difference between coloured and uncoloured samples of the salt. Such a difference has not yet been reported.

Another point to be raised is why are the sylvines, which contain helium, presumably from α-decay, and a much larger source of available energy from ^{40}K, not coloured? It may be that here the difference in ease of coloration and stability of the colour produced is coming into play (Wieninger, 1953, p. 155), but again this seems unlikely since no outstanding difference in these properties between potassium chloride and sodium chloride has been observed.

Whilst speaking of the sylvines, it is of interest to note that the coloured rocksalt invariably occurs in close proximity to sylvine (Johnson, R. Odertal, private communication). It is, apparently, a maxim in the salt mines that wherever coloured rocksalt occurs sylvine is to be found near at hand. This being so, one might expect the layers of rocksalt near sylvine to contain relatively more potassium than the rest of the layer, since here the first crystallisation of sodium chloride would overlap the last of the potassium chloride. This might provide an optimum concentration of foreign matter for sensitisation. Alternatively, a greater concentration of potassium would also mean a correspondingly larger source of irradiation.

The generally higher level of impurity in sylvines is also to be noted. Since an optimum concentration of divalent impurity for sensitisation towards colour centre formation has been observed, it is probable that above a certain limit of divalent impurity concentration, the tendency to form colour centres is prohibited, at least in this case where only relatively weak sources are considered. This may explain why all the salt in the secondary deposit is not coloured and also why the sylvines are not coloured. In order to explain why the primary rocksalt is not coloured, one must refer to the sources of irradiation available for the purpose. This is exemplified in the vastly different helium contents between primary and secondary, assuming that all helium is radiogenic. Indeed, the only difference between the primary and secondary deposits available at present, which might provide a clue as to why the one is coloured and the other not, is in the helium contents. No regular difference can be observed in the lead contents, however.

Further, Przibram (1951), Born (1936), and Valentiner (1912) find a correlation to exist between helium content of the coloured rocksalts and their colour and we have obtained samples of blue, violet, and yellow rocksalt from Wintershall for examination of helium contents in this laboratory.

It will be clear however from this review, that no attempt has, as yet, been

made to carry out a complete set of experiments on one and the same sample of material or even on different samples from the same locality.

It was proposed, therefore, to use salts from Wintershall for an investigation of:

1. The helium content of the salts with a view to finding a correlation between helium content and colour, if such a correlation exists.

2. The impurities present in rocksalt with a view to detecting a sensitiser for colour formation.

3. Diffusion of helium in rocksalt.

4. The origin of helium is rocksalt, by examination of uranium and thorium contents. (It was proposed also to grow salt crystals in the laboratory and measure the amounts of helium occluded.)

5. The absorption spectra of the various coloured samples. (A few results for the helium content of several salts from the Grimberg Mine in the Werra Valley are also included.)

2. Microdetermination of Helium in Rocksalts

Experimental

The apparatus constructed for this research followed the pattern of that described by Glückauf (1946). Recent modifications are described by Chackett, Reasbeck and Wilson (1953).

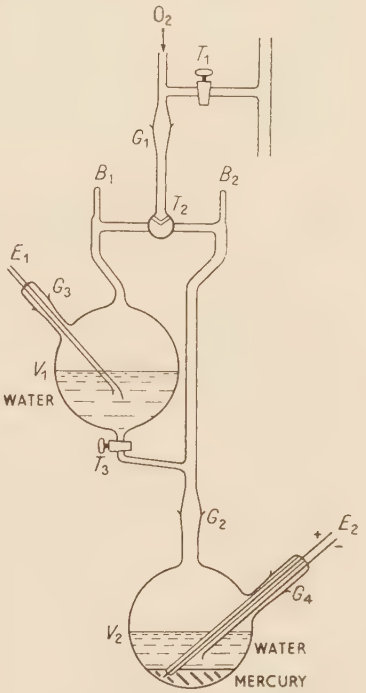

Fig. 1.

The apparatus consists of a glass vessel wherein the gases contained in the salts are liberated through solution in water. A source of helium free oxygen is supplied to this vessel to act as a "carrier" gas and effect the complete removal of other gases from solution. The gases freed in this way along with the excess oxygen, are transferred into a closed system where they are circulated over heated palladium, which serves to remove gross quantities of hydrogen as water. The remaining gases are transferred from the circulating system to a gas fractionating column. The helium which emerges from this column is admitted to a Pirani gauge which is calibrated each time with measured quantities of spectroscopically pure helium. 10^{-6} to 10^{-7} cc of helium at N.T.P. were measured with an accuracy of better than 1%. Determination of the helium content of air served as a speedy check on the correct functioning of the apparatus.

The dissolving apparatus is shown in Fig. 1. It consists of two inter-connected glass vessels V_1 and V_2 of about 250 ccs capacity which can be attached to the main apparatus at the standard ground joint (B19) G_1. V_1 and V_2 may be pumped down to vacuum simultaneously through taps T_1, T_2, and T_3, or independently, if it is necessary to keep T_3 closed, through T_1 and T_2. V_2 may be removed at will to reject old samples and replace with new, through the standard ground joint (B19) G_2.

The mode of operation is as follows:

The apparatus is attached at the ground joint G_1 and evacuated with both V_1 and V_2 empty.

Air is then admitted into the dissolving apparatus by breaking one of the two inlets B_1 and B_2. V_2 may now be removed readily, a weighed sample of rocksalt inserted, and the flask replaced. Then with tap T_3 closed 100–150 ccs of distilled water, containing a little sulphuric acid to

facilitate electrolysis, are admitted into V_1 through B_1. B_1 and B_2 are then sealed and V_1 and V_2 evacuated through the two-way tap T_2.

After the initial evacuation of V_1 complete removal of rare gases from the water is achieved by vigorous electrolysis using the platinum electrodes E_1, which are attached to V_1 through the ground joint (B14) G_3 and are connected to a 24 volt, D.C. supply. Experiment showed that if the water is electrolysed for a period of one minute and the electrolytic gases pumped away, then this procedure, when repeated 6–7 times, is sufficient to remove substantially all the rare gases in solution in the water. A blank experiment on the water, using 2 to 3 times the amount of oxygen used in actual experiments, gave a helium value of 1×10^{-8} ccs helium. In an actual experiment, this is less than one per cent of the total helium measured.

Having successfully removed the helium from the solvent to be used, tap T_3 may now be opened and some of the water allowed to run into V_2 which contains the rocksalt sample. Stirring to facilitate the dissolution process is achieved in V_2 by a small iron nail sealed in a *Pyrex* glass envelope which is made to rotate by the use of an external magnetic stirrer. Sufficient water is generally accommodated in V_1 for at least three experiments.

When the solution of the rocksalt sample is complete, the gases so liberated may be freed from solution in the brine in the same way as before, i.e. by electrolysis using the platinum electrodes E_2 which enter V_2 through the ground joint G_4. A mercury anode was used for the removal of chlorine.

With each successive operation of electrolysis, oxygen was added to about 1 cm pressure to the electrolytic gases and the gases transferred to the cooled charcoal unit in the circulating system. Here the hydrogen produced electrolytically was removed, in excess oxygen, as water.

It was found in a test experiment on the solution remaining after the gases had been liberated by 6–7 operations of electrolysis, that substantially all the helium had been removed from the solution. In a trial experiment using more oxygen than is generally used in an experiment, only 1×10^{-8} ccs helium were detected in the solution which remained.

All the measurements on rocksalts, the results of which are given below, were carried out in the manner described.

Results, and discussion of helium contents

The results from the various samples examined together with their place of origin are given in chronological order in Table 1.

The pieces referred to in Table 1 under the column headed "Physical State" were in general less than 1 cm^3 in size and were obtained by fracture of a larger single piece. It will be observed that, with a few exceptions, the helium content of the samples apparently decreased with time although this effect could be due to inhomogeneity in the samples; diffusion of helium out of the salts is also a possibility. A sample of violet salt was therefore ground and thoroughly mixed and analysis made of the helium content of samples of the salt, over a period of two weeks. The results obtained in chronological order, 6, 7, and 8, indicate loss of helium, and a study of the diffusion of helium out of rocksalts will be published shortly (Thomson and Wardle). The value of the diffusion coefficient at 25°C was found to be 3.0×10^{-15} cm^2/sec. If the rocksalt layers are regarded as homogeneous diffusion media several metres thick, then diffusion of helium out of the salts in 10^8 years would be negligible.

With regard to the question raised by Przibram regarding helium content and colour, these results show that there is definite justification for saying that a correlation does exist between helium content and colour.

Thus the helium content of the salts from Wintershall shows a change from blue to yellow to violet, the blue having the highest helium content and the violet the least. The salts from Grimberg are similarly arrayed as far as they were examined, the yellow variety having a higher helium content than the violet, a result expected by Przibram (1953, p. 137).

Table 1

No.	*Place of Origin*	*Colour*	*Physical State*	He *ccs/gm* $\times 10^7$
1	Wintershall, Herringen, Werra Valley	Yellow	Pieces	2·47
2	Wintershall, Herringen, Werra Valley	Yellow	Pieces	1·85
3	Grimberg Mine, Werra	Violet	Pieces	1·00
4	Grimberg Mine, Werra	Violet	Pieces	0·36
5	Grimberg Mine, Werra	Violet	Pieces	0·26
6	Wintershall	Violet	Powder	0·89
7	Wintershall	Violet	Powder	0·78
8	Wintershall	Violet	Powder	0·72
9	Wintershall	Yellow	Pieces	4·58
10	Wintershall	Yellow	Pieces	4·00
11	Wintershall	Yellow	Pieces	7·09
12	Wintershall	Blue	Pieces	15·0
13	Wintershall	Blue	Pieces	20·4
14	Wintershall	Blue	Pieces	12·4
15	Grimberg	Yellow	Pieces	15·1
16	Grimberg	Yellow	Pieces	21·5

Accuracy $\pm 1\%$.

3. Occlusion of Helium During Crystal Growth

Many salts trap small quantities of mother liquor on crystallisation, especially if crystal growth is slow (Winchell, 1927), and our specimens of coloured rocksalt have been found to contain occluded liquor; this can be seen on cleaving the crystals. We have considered the possibility that this occluded brine may be responsible for some of the helium in the salts.

Helium is appreciably soluble in water (Landolt-Börnstein, 1905, p. 601) and in salt solutions (Akerlöf, 1935), and Urry (1935) has measured the helium plus neon content of sea water at different depths, finding 12 to 20 $\times 10^{-5}$ cc/litre. Taking the most favourable case that the "helium plus neon" is all helium, each gram of rocksalt would have to trap 0·05 cc brine to account for a helium content of 10^{-8} cc/g. In the case of the primary rocksalt this helium content agrees with the observed values (Born, 1934) of about 10^{-8} cc/g.

We have grown crystals of rocksalt, over a period of a month, in air saturated water and we find in them 5×10^{-9} cc/g helium. It seems therefore that this might account for the origin of at least some of the helium in the primary rocksalts.

In the case of the secondary rocksalts crystallisation has probably occurred in water enriched in radium and therefore in helium. The solubility of helium is high

at higher pressures (Akerlöf, 1935) and it is known that the gas from borings in Germany is enriched in helium (Wager, 1935). The helium concentration may be between 2 and 3500 times that of the atmosphere. Such enrichment might mean considerable concentrations of helium in the "deep natural waters" whence the salts have crystallised.

Neon has not been detected in any of the secondary salts examined in this laboratory, and since it has no radioactive origin, cannot have become enriched in the primary or secondary layers.

In the potassium salts examined by Smits and Gentner, and Aldrich and Nier (Smits and Gentner, 1950; Aldrich and Nier, 1948), up to 30% of the argon they found was of atmospheric origin and not of radiogenic origin. The data available on the solubility of argon in salt solutions suggests that only 0·07 cc/g brine need be trapped in potassium chloride to account for the argon in the samples with the lowest percentage atmospheric argon. This is not an unreasonably large amount of liquid (Thorpe, 1929).

A consequence of such a trapping mechanism would be that the primary rock-salts might contain 10^{-5} to 10^{-6} cc/g argon.

4. Absorption Spectra of the Salts from Wintershall

The absorption spectrum of each of the coloured varieties has been measured for us by Dr. R. V. Hesketh to whom we are very much indebted. These are reproduced in Fig. 2.

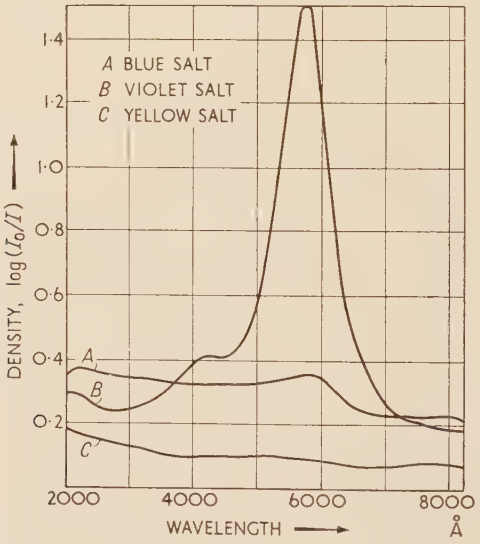

Fig. 2.

The violet sample shows a strong absorption maximum at 5750 Å which is taken to be the R 11 band, with other weaker maxima at 2000 Å and 4100 Å. The latter may be attributed to impurity as is done by Przibram in other cases for

maxima around 4400 Å. A maximum in this region has only been observed previously in the blue salts.

The blue sample shows maxima at 5800–6000 Å, which may be the *R*-band again or colloids or a combination of the two, and, like the violet, at 2200 Å.

The yellow sample unfortunately faded before a measurement could be made, conforming to the general lability of the centres in natural yellow varieties (Przibram, 1953, p. 117) examined by other workers. Even in the colourless samples so produced a tendency for the absorption to increase around 2000 Å is to be observed, however, thus making the interpretation of the "maxima" in the violet and blue cases in this region as *V*-bands somewhat dubious.

5. Impurities in the Wintershall Rocksalts

In order to explain why all samples of rocksalt are not coloured, one must assume that in the cases of the ones that are coloured, some impurity is present, which sensitises the salt towards colour formation. Sulphide ion, for example, has been suggested by Wieninger as a sensitiser for colloid formation as is found to be the case in the silver halides. The various samples from Wintershall have therefore been subjected to spectrographic examination to see if any significant difference exists in chemical content between them. The results are shown in Table 2. These will be discussed later.

Other elements not detected in any of the samples were: As, Au, Ba, Be, Bi, Cd, Co, Cr, Ga, Ge, Hg, In, Li, Mo, Sb, Ti, Tl, W, Zn, Zr.

Table 2

	Yellow %	*Violet* %	*Blue* %
Potassium	0·05	0·03	0·50 app.
Lead	0·0001*	—	0·0001
Calcium	0·001	0·001	1·0 app.
Copper	0·00005	0·02	0·0001
Magnesium	0·005	0·002	>0·1
Strontium	—	—	0·02
Iron	0·0005	0·0002	0·002
Silicon	trace	—	0·002
Rubidium	—	—	0·0005
Manganese	0·0002	0·0001*	—
Nickel	0·0001*	0·0001	0·0002
Silver	0·001*	0·0001*	—
Aluminium	trace	trace	trace

* = upper limit.

6. The Uranium and Thorium Content of Blue Rocksalt

In view of the fact that natural rocksalt appears to contain "excessive" quantities of helium, it is surprising that no reports have been published about investigations on their thorium as well as their uranium content.

The thorium and uranium contents of a sample of rocksalt have now been determined for us by Dr. J. C. Dalton, to whom we are most grateful. A large piece of blue rocksalt was broken up into smaller pieces and the smaller pieces were thoroughly mixed and quartered. Uranium and thorium analyses were then carried out by the most sensitive methods available, i.e. uranium by the fluorescence method and thorium by scintillation counting, on 200 gm samples of the smaller pieces.

(*a*) *Uranium* [*cf.* Dalton *et al* (1953), Thomson *et al* (1954)]

200 g of rocksalt were dissolved in about 1½ litres of distilled water and hydrochloric acid added to make the solution approximately 1 N with respect to acid. 60 mg of aluminium were added, as chloride, to this solution and carbonate-free ammonia gas passed into the solution till precipitation occurred. The precipitate was collected by centrifugation.

The precipitate of aluminium hydroxide was dissolved in nitric acid and re-precipitated with ammonia gas to free it from chloride. This precipitate was then dissolved in 20 ml of concentrated nitric acid and 10 to 20 g of solid ammonium nitrate added to the solution.

The solution was then shaken with four separate portions of ether (20 ml each time) to extract the uranium. All the ether was removed from this extract by heating on a water-bath in the presence of 100 ml of water, and the volume of water was then reduced cautiously to less than 10 ml.

The resulting solution was made up to 10 ml with water and 1 ml portions evaporated to dryness in platinum fluorimeter trays. 0·94 g of sodium fluoride were added, the solids fused and the resulting phosphors examined in a fluorimeter.

Blank sodium fluoride phosphors were prepared so that the difference in fluorimeter readings represented the uranium present.

(*b*) *Thorium* [*cf.* Dalton *et al* (1953), Thomson *et al* (1954)]

200 g of rocksalt were dissolved in about 1½ litres of distilled water and hydrochloric acid was added to make the solution approximately 1 N with respect to acid. 100 mg of iron were added as chloride.

The precipitate obtained on passing carbonate-free ammonia gas into this solution was dissolved in 50 ccs of concentrated hydrochloric acid, producing a solution which was 6·5 N with respect to acid. This solution was shaken four times with 50 ml portions of ether equilibrated with 6·5 N hydrochloric acid till the solution was almost free from iron. 5 mg of iron were then added as chloride and the ether in the aqueous phase evaporated on a water bath. The total volume of solution was reduced to 20 ml and then it was diluted with 20 ml water to give a solution which was approximately 2 N with respect to hydrochloric acid.

Carbonate-free ammonia gas was passed into this solution. The small precipitate of ferric hydroxide produced was collected and re-dissolved in 25 ml of 0·2 N hydrochloric acid. This solution was stored for one month, to allow ThX to grow to radioactive equilibrium. 2 mg of lead were then added as acetate. Hydrogen sulphide was passed into the solution and the resulting precipitate of lead sulphide with Th(B + C) collected and re-dissolved in the minimum amount of warm concentrated hydrochloric acid. This solution was evaporated to dryness on a *Polystyrene* scintillation counter disc and α-particle counting started 45 minutes after precipitation. The scintillation counter used has already been described: the background count was 1 per hour only.

The ThC α-particles (in equilibrium with parent ThB half-life 10·6 hours) were counted over a period of 16 hours. Subtraction of the 16 hour background count then gave the thorium present. This was compared with a standard source.

The quantities measured in this way were: $0.17 \pm 0.02 \times 10^{-9}$ g U/g salt and less than 2×10^{-9} g Th/g salt.

It can be seen that the uranium and thorium values are extremely small and

these elements would not contribute much to the amounts of helium found in the salts. Most of the helium must certainly arise then, through some process other than uranium and thorium decay. If the uranium and thorium contents of the primary salts are about the same, then in 10^8 years they would contain $0{\cdot}8 \times 10^{-8}$ cc/g. The observed values (Born, 1934) are about 1×10^{-8} cc/g.

7. Thermal Bleaching of the Colours in Rocksalts

Both the violet and blue samples were subjected to an increase in temperature in daylight and they were found to bleach to a colourless state well below the melting point. The experiment was carried out in only a qualitative fashion to make sure that these samples conformed, in behaviour to heat, with samples examined by other workers. The violet salts showed thermoluminescence when heated in the dark.

The yellow colour was also found to fade quite rapidly on exposure to daylight without having to increase the salt temperature. This again agrees with the general behaviour of natural yellow irradiation-coloured rocksalt observed by other workers and also with artificially irradiation-coloured samples of purer sodium chloride.

8. Discussion of the Results

The results of the helium measurements shown in Table 1 indicate a correlation between helium content and colour of the sample under examination. This would indicate that the coloration achieved in any sample depends at least in part on the amount of α-irradiation which that sample has received. The distribution in striae of the colour in the blue and the violet rocksalts suggests localised irradiation or sensitisation. If Hahn's hypothesis is accepted this could be due to the growth of radium D in the crystallisation process along crystal boundaries. Subsequent α-activity from the radium F arising from the radium D should produce high concentrations of F-centres in the immediate vicinity. Such high local concentrations of F-centres would favour their aggregation into secondary units such as the R- and M-centres which occur in the violet and blue varieties, or even colloids.

Bombardment of sodium chloride (and other alkali halides) with high energy α-particles or electrons has been observed to produce initially a high concentration of F-centres. On thermal or optical bleaching a violet colour develops and the crystal now shows an absorption maximum at 5800 Å (Westervelt, 1952a, 1953; Przibram, 1951b). This absorption band has been attributed to colloids (Scott and Smith, 1951; McLennan, 1951) or sodium at interstitial sites (Westervelt, 1952b) arising as a result of radiation damage to the crystal. No precise evidence for such designations has been put forward but it is to be noted that no colloids were detected by Wieninger in similar experiments.

The similarity of this band at 5800 Å to those which occur in the natural violet rocksalt is striking, however, and strongly supports the view that polonium α-particles are the prime movers in producing this coloration in nature.

That irradiation amount is not the only factor entering into the coloration process is evident from the helium values found for the yellow varieties. Thus, if irradiation were the sole effect, one would expect the blue variety, which contains

the higher aggregates of centres, i.e. colloids, to have the highest helium content, the violet, the next highest helium content, since this also contains secondary centres, and the yellow variety, containing only F-centres, to have the lowest helium content. The helium values actually found indicate the order of helium contents to be blue the highest, then yellow, and the violet the least. Thus one must postulate in the case of the violet salt that there is some form of sensitisation towards centre formation and also towards aggregation of these centres. This being so, it is reasonable to assume that there is also sensitisation in the other cases, though not necessarily to the same degree. Thus, the yellow variety with less sensitisation than the violet, requires a greater amount of irradiation in order to achieve its colour.

By considering the joint effect of irradiation and sensitisation, one can account satisfactorily for the variation in helium content amongst the various coloured specimens. Similarly, in order to explain why uncoloured samples, which contain quantities of helium of the same order of magnitude as the coloured samples, are not coloured, one must assume that these samples are not sensitised to the same degree as are the coloured varieties.

It can be seen from the results of the spectrographic analysis (Table 2) that the samples differ widely in their content of small quantities of impurity, so much so that it is difficult to identify any single impurity as a likely sensitiser. It is, however, notable that the blue sample, in which colloids occur, is much less pure than the violet or yellow samples. The level of divalent impurity in the violet salt is greater than that of the yellow, and this suggests that in the violet salt there has been greater sensitisation. Though the helium content of the violet is less than that of the yellow salt, the increased sensitisation of the violet salt could account for the colour. It is also noteworthy that the yellow and blue samples, which on the basis of helium content have received the greater amount of irradiation, also contain the greater lead content and that they both contain higher quantities of potassium than does the violet, indicating that here too by ^{40}K decay they have also received the greater irradiation.

The general level of divalent impurity is greater in the violet and blue samples than in the yellow, the extremely high calcium content of the blue, and the high copper content of the violet salt being noteworthy. The copper content for the yellow and blue salts agrees well with the value previously found by Biltz and Markus for a sample of blue rocksalt (Biltz and Markus, 1909).

The absence of lithium in any sample is also noteworthy in view of the fact that lithium has been detected in "deep natural waters" which have been taken as similar to those from which the salts crystallised. Too much significance must not be attached to this fact since the actual concentration of lithium in waters is not recorded and may be at such a low level as to be not detectable in these analyses.

9. The Sensitisation of Naturally Occurring Sodium Chloride Towards Colour Formation

Two cases are considered, firstly sensitisation by divalent negative ions and secondly sensitisation by divalent positive ions. Sensitisation by plastic deformation is ignored mainly because of the lack of knowledge of the history of the deposits.

Sensitisation by divalent negative ions

It has been shown in the case of the fluorites, whose coloration is attributable to some radio-active influence, that the depth of colour attained is intimately connected with the sulphur content of the sample (Steinmetz, 1923, 1925). It has also been suggested that the formation of sensitivity specks in silver halides containing traces of silver sulphide, is due to the aggregation of *F*-centres arising from the inclusion, substitutionally, of S^{-} in the halide lattice. Collodial silver particles are thought to result from the further aggregation of *F*-centres (Mitchell, 1949).

On the basis of these facts, it has been suggested that sulphide ion is the sensitiser responsible for the appearance of colloidal aggregates in the naturally occurring rocksalts (Wieninger, 1951). In making this suggestion, Wieninger has assumed that since the two types of halides, i.e. sodium and silver, are of similar crystalline form, then what applies to the one may well apply to the other. The two cases, however, are not strictly analogous. The basis of the argument for the silver halide case is that $S^{=}$ is incorporated in the lattice as substitutional S^{-} plus an *F*-centre. The presence of *F*-centres is then thought to aid formation of colloidal silver by aggregation. In the case of the rocksalts, this cannot be so, for after bleaching by heat treatment *F*-centres should be re-generated and the crystal become coloured yellow. The bleaching, in fact, is quite permanent in the absence of suitable irradiation. One must assume, therefore, that the inclusion of sulphide ion in rocksalt is not by the same mechanism as that postulated for the inclusion in silver halides. This, however, does not preclude the possibility of $S^{=}$ being a sensitiser toward centre formation under the influence of irradiation.

Since, for these reasons, it seems unlikely that $S^{=}$ enters the sodium chloride lattice as S^{-} plus an electron, then assuming the inclusion to be substitutional, it must enter as $S^{=}$ with an associated anion vacancy. Inclusion of $S^{=}$ would thus increase the concentration of trapping centres for electrons released by irradiation and therefore sensitise the crystal toward *F*-centre formation. This should result in greater saturation values of *F*-centres and thus favour their aggregation. Sensitisation towards the formation of colloids should also result.

Mitchell has pointed out that the affinity for a sulphur atom to take up a second electron in forming $S^{=}$ is much less than the affinity for a chlorine atom to take up an electron and form Cl^{-}. Without reference to lattice energies or the mode of inclusion of $S^{=}$ in sodium chloride, it would seem probable that on irradiation of sodium chloride containing sodium sulphide an electron would be more readily given up by $S^{=}$ than by Cl^{-}. It must be borne in mind that in the naturally occurring rocksalt, one is considering relatively weak irradiation sources acting over a long time. Such an effect would also sensitise the salt toward *F*-centre formation.

If indeed the electrons available, for the formation of *F*-centres, are derived from $S^{=}$ then the characteristic *V*-band need not be present in the natural irradiation coloured rocksalt. It would be of interest to examine further the absorption spectrum of the natural salts in the *U*–*V* region to confirm whether or not the *V*-band is actually present. Unfortunately, the absorption spectrum measured in

this region and shown in Fig. 2 is not sufficiently accurate to make this point certain but the indication is that the V-band is absent.

Sensitisation by divalent positive ions

It has been seen above that sensitisation towards colour formation can be achieved by inclusion of a divalent negative ion and it may seem anomalous that divalent positive ions should produce the same effect. It must be remembered however that there are two possible fates for the secondary electrons which are released as a result of the incident irradiation. Firstly the electron may combine with an anion vacancy forming an F-centre, the chances of this process occurring being favoured by the number of anion vacancies available. Alternatively, the electrons may re-combine with the free holes from which they were originally released. Formation of F-centres will then be favoured by increasing the number of trapping centres for the free positive holes. There is good reason to believe, in certain cases, e.g. the alkaline earth elements, that divalent positive ions enter the sodium chloride lattice substitutionally accompanied by a cation vacancy (Haven, 1953; Maurer, 1950; Koch and Wagner, 1937; Pick, 1939; Seitz, 1951; Schulman *et al.*, 1952, 1953). Inclusion of these divalent positive ions then will increase the number of trapping centres for positive holes and should therefore sensitise the crystal towards F-centre formation.

In addition to the qualitative observation of sensitisation it has been observed that for some divalent positive ions, at least, an optimum concentration of divalent ions for sensitisation occurs. In this case one must assume that initially the two Cl^- which accompany the positive ion form fresh additions to the lattice without affecting the number of anion vacancies. At the optimum the limit to this process is reached and the Cl^- must then begin to occupy anion vacancies and thereby reduce the tendency to centre formation on irradiation.

Alternatively, it may be that at the optimum the concentration of divalent positive ions is such that clustering becomes favoured. This would tend to increase greatly the local concentration of cation vacancies in the vicinity of the clusters but reduce it generally in the rest of the crystal. Such a process could then lead to relatively less sensitisation at concentrations greater than the optimum.

If the free holes are indeed captured at cation vacancies associated with divalent positive ions, then one would expect the characteristic V-band to be modified somewhat by virtue of the presence of the divalent positive ion. Such an effect has been observed with the F-band in potassium chloride when the environment of the electron trapped at the anion vacancy has been modified by virtue of the presence of Rb^+ (Gnaedinger, 1953). Further investigation of V-bands associated with divalent impurity is indicated and may lead to the actual form which sensitisation takes in the naturally coloured rocksalts.

It is interesting to note in this respect that no less than six R-bands have been observed in a crystal of sodium chloride after irradiation with x-rays or electron bombardment, with maxima at 6600, 6200, 5960, 5720, 5520, and 5260 Å (Uchida and Yagi, 1952). It may be that the presence of impurity ions in substitutional positions in the lattice is responsible for some of these bands and this suggests further investigation along these lines.

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The distribution of germanium among coexisting phases of partly glassy rocks

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ABSTRACT

The coexisting mineral and glass phases of five glassy rocks containing phenocrysts, have been separated and their germanium contents determined. The results show that during crystallization, germanium substitutes for silicon preferentially in neso- and inosilicates, and is impoverished in tectosilicates.

Introduction

Though the geochemical distribution of germanium has been investigated in some detail by Goldschmidt and Peters (1933), and it has been shown that germanium replaces silicon in silicate lattices (Goldschmidt, 1931), it is not known conclusively which type of silicate structure is entered preferentially.

Wickman (1943) pointed out that there seemed to be some concentration of germanium in those minerals with isolated silicate tetrahedra as compared with more linked silicates. Since the germanium content depends on the geochemistry of the parent rock as much as on the structure of the individual mineral, pairs of coexisting minerals from the same localities were analysed for Wickman. In most cases, the silicate with the less-linked structure had the higher germanium content. However, the evidence was not conclusive and as Wickman said: "The question as to the distribution of germanium among the silicates in a certain association is naturally of great interest. An investigation of the germanium content of all the minerals from a single occurrence with a determined paragenesis should thus give significant results."

This investigation was to test Wickman's views by the determination of the germanium contents of coexisting silicates from partly glassy rocks.

The Value of Glassy Rocks in Investigations of this kind

It was at the suggestion of Dr. H. Neumann that the examination was made of partly glassy rocks. In studying element distribution among coexisting minerals, it is important to select material in which the different mineral phases have crystallized at the same stage, when their compositions approached equilibrium with each other and with their parent liquid. For the present purposes no valid conclusions can be drawn from data based on minerals formed at different stages of the crystallization of the parent liquid, and whose compositions are not interdependent.

The distribution ratios due to crystallization are likely to be preserved only in synthetic melts and in those rocks formed by rapid chilling before differentiation

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could proceed very far, i.e., glassy rocks in which the equilibrium has been frozen. The latter have the advantage that a definite range of composition of the parent liquid during which the minerals crystallized, can be determined. This is bounded at one end by the bulk composition of the rock (the original magma), and at the other by that of the residual glass (the derived magma). The greater the proportion of glass, the narrower will be the possible range in composition of the parent liquid.

From analytical data on partly glassy rocks and their constituent phases, the distribution ratios for the elements between the liquid and crystals can be derived.

Criteria of suitable rocks for an investigation of this type are:

(a) Each rock should contain as large a number as possible of mineral species available for analysis.

(b) The mineral phases should have formed slowly, so that they approached equilibrium with each other and with the magma (i.e., they should occur as phenocrysts with a minimum of non-equilibrium structures such as zoning, reaction rims, etc.).

(c) The distribution relationships of a definite stage in consolidation should be preserved in the rock, i.e., the equilibrium should be frozen and the magmatic liquid preserved as glass.

Description of Material Analysed

Five glassy rocks and one assemblage of weathered-out phenocrysts were investigated, most of the samples being from the collections of the Department of Geology, University of Leeds. The first four were selected, and much of their preliminary treatment done by Dr. H. Neumann, at that time of the Department. A fuller description of the rocks and their treatment can be obtained elsewhere (Harris, 1952).

(1) "Pitchstone, Glen Shurig, Arran, Scotland." The rock, described by Scott (1915) and Tyrrell (1928), contains over 80% of glass, 11% plagioclase, 3% quartz, about 2% each of olivine and clinopyroxene, and minor amounts of iron ores.

(2) "Phenocrysts from Odawara, Hakone Volcano, Japan" were from a pumice in which the pumiceous ground-mass had decomposed leaving unaltered phenocrysts of hypersthene, augite, plagioclase, iron ores, and a little olivine. The material was presented by Professor H. Kuno.

(3) "Hypersthene-augite-dacite-pumice, Odawara," also donated by Professor Kuno, contained about 80% glass, 16% plagioclase, 4% pyroxene, a little iron ore, and minute amounts of olivine.

(4) "Pitchstone, Ardnamurchan, Scotland," from S.S.E. of Ben Hiant summit, is probably the same as that described in the Ardnamurchan Memoir (Richey, 1930, pp. 122, 127). It contains 82% glass, 13% plagioclase, 3–4% pigeonitic pyroxene, and 1½% iron ores.

(5) "Andesite, Ngauruhoe, New Zealand." The sample, provided by J. J. Reed, N.Z. Geological Survey, was erupted from Ngauruhoe in February, 1949. It contained about 7% of ortho- and clinopyroxenes, 23% of plagioclase, and a minute amount of olivine (0·1%). The ground mass may have been devitrified, since the rock is an ejected block, no doubt reheated at the time of ejection ($H_2O = 0{\cdot}10\%$).

(6) "Pitchstone, Judd's No. 1 dike, Tomore Shore, Arran," was a very acidic type of pitchstone, with 95% glass, 2% quartz, 2–3% feldspar, and 0·5% of clinopyroxene, olivine, and iron ores.

In the pitchstones, the olivine was fayalite ($Fo_{12}Fa_{88}$ and $Fo_{11}Fa_{89}$), and in the dacite and andesite, the minute amounts (0·1%) of olivine were Fo_{73} and Fo_{63} respectively.

Table 1. *Results of germanium analyses (in P.P.M.)*

Rock	*Glen Shurig Pitchstone*	*Odawara Phenocrysts*	*Odawara Dacite Pumice*	*Ardnamurchan Pitchstone*	*Ngauruhoe Andesite*	*Judd's No.* 1 *Dike Pitchstone*
Rock Ge content	1·62, 1·40, 1·27, 1·60		1·64, 1·68	1·26, 1·31 1·49, 1·46	1·37, 1·39 1·39	1·34, 1·47
Glass Ge content	1·57, 1·63, 1·59, 1·40		1·93, 1·96	1·27, 1·30 1·22, 1·28	1·48, 1·40, 1·29	1·53, 1·37, 1·56 1·47, 1·50, 1·72, 1·39
Magnetite Ge content	2·52	0·65, 0·60	0·94, 1·18	1·50, 1·39		2·37
Ilmenite Ge content				0·43		
Olivine Ge content	2·52, 2·99, 2·98	1·43, 1·17			1·48	3·43
Orthopyroxene Ge content		2·76,2·63		2·47, 2·50 (pigeonite)	3·36, 2·64 2·81, 2·48 (mixed pyroxenes)	
Clinopyroxene Ge content	4·88 4·33 4·01	2·76, 3·07	2·15, 2·36			3·77
Feldspar Ge content		0·94, 0·84	0·81, 0·90	0·91, 0·96	0·60, 0·81	
Quartz-feldspar mixtures Ge content	Fraction (a) = 0·96, 0·75, 0·95 Fraction (b) = 1·04, 0·78					Fraction A = 0·58, 0·66 Fraction B = 1·60, 1·79

Table 2. Germanium-silicon ratios

	Ge *content* (*p.p.m.*)	SiO_2 *content* %	Ge *atoms/ million* Si *atoms*
Glen Shurig Pitchstone			
Rock	1·47	71·9	1·69
Glass	1·55	73·5	1·75
Olivine	2·83	30·3	7·72
Clinopyroxene	4·4	48·6	7·49
Quartz-feldspar mixtures	0·90	78·8	0·93
Odawara Phenocrysts			
Olivine	1·3	36·8	2·92
Orthopyroxene	2·7	51·5	4·33
Clinopyroxene	2·9	52·9	4·53
Feldspar	0·89	51·8	1·42
Odawara Dacite			
Rock	1·66	64·8	2·12
Glass	1·95	69·0	2·34
Clinopyroxene	2·25	51·5	3·62
Feldspar	0·85	51·3	1·37
Ardnamurchan Pitchstone			
Rock	1·38	66·5	1·72
Glass	1·27	71·6	1·46
Pigeonite	2·48	49·0	4·19
Feldspar	0·94	58·3	1·33
Ngauruhoe Andesite			
Rock	1·38	57·0	2·00
Glass	1·39	59·4	1·94
Olivine	1·48	37	3·3
Mixed pyroxene	2·82	52·2	4·47
Feldspar	0·70	51·3	1·13
Judd's No. 1 *Dike—Pitchstone*			
Rock	1·40	73·2	1·58
Glass	1·50	73·4	1·69
Olivine	3·43	27·9	10·2
Clinopyroxene	3·77	45·5	6·9
Quartz-feldspar mixture (*A*)	0·62	84·3	0·6
Quartz-feldspar mixture (*B*)	1·70	76·0	1·85

Table 3. Germanium contents relative to silicon

(All values in Ge atoms/1,000,000 Si atoms)

	Ngauruhoe Andesite	*Odawara Phenocrysts*	*Odawara Dacite*	*Ardnamurchan Pitchstone*	*Glen Shurig Pitchstone*	*Judd's No. 1 Dike Pitchstone*
Rock	2·0		2·1	1·7	1·7	1·6
Glass	1·9		2·3	1·5	1·7	1·7
Olivine	3·3	2·9			7·7	10·2
Clinopyroxene	4·5	4·5	3·6		7·5	6·9
Orthopyroxene		4·3		4·2		
Feldspar	1·1	1·4	1·4	1·3		
Quartz-feldspar mixture					0·9	0·6 1·85

From these values can be derived enrichment values for each mineral species, relative to glass,

i.e. $\frac{\text{Concentration Ge in mineral (relative to Si)}}{\text{Concentration Ge in magma (relative to Si)}}$

Olivine	1·7				4·5	6·0
Pyroxene	2·4		1·6	2·8	4·4	4·1
Feldspar	0·58		0·61	0·87		
Quartz-feldspar mixture					0·53	0·35 1·1

Preparation of Material Analysed

The six rocks were separated into their constituent phases by the use of heavy liquids (acetylene tetrabromide and Clerici solution) and subsequent magnetic separation. With such fine-grained rocks the incidence of composite grains was too high to permit clean separation by the use of methods based on one physical property alone.

Magnetic separation was done with permanent magnets and with an electromagnetic separator of the type described by Officer (1947). This instrument functioned by the deflection of mineral grains falling through an inhomogeneous magnetic field, and though not as efficient as the Frantz "Isodynamic" separator, its construction was comparatively simple.

After gravity and magnetic separation, residual impurities were removed by hand. Even with the utmost care, the feldspars from the Glen Shurig and Judd's No. 1 dike pitchstones could not be isolated from quartz, each containing about 50% of quartz.

The identities of the mineral species were checked by optical and x-ray powder methods.

Method of Analysis

The method of spectrochemical analysis for germanium of the rocks, glasses, and minerals is described elsewhere (Harris, 1952, 1954). The lower limit of estimation was less than 0·1 microgram or 0·1 p.p.m. in a one gram sample, and the accuracy was about $\pm 10\%$.

All rocks, glasses, and silicate minerals were analysed chemically for their major constituents.

Results of Analysis

The results of the germanium estimations using the spectrochemical method are given in Table 1. Where possible, determinations were done in duplicate, and when these results disagreed, were repeated. In some cases, especially among the olivines, there was insufficient material to allow more than one estimation, and that, often on too little material.

The germanium contents of the silicate minerals, rocks and glasses are presented in Table 2 to give a comparison of the relative atomic abundances of germanium and silicon.

The results are retabulated in order of decreasing silica content of the parent rocks in Table 3.

In addition to the foregoing, a group of minerals separated from a hypabyssal rock were analysed for germanium. These minerals, separated and kindly made available by Mr. O. von Knorring of this Department, were from an alkaline ultrabasic rock, aillikite, from Aillik Point, Labrador. The minerals were of interest because they included, in addition to olivine, biotite and the non-silicates magnetite, apatite and calcite, the calcite constituting the ground-mass of the rock. The results are shown in Table 4.

Since the intrusion is of such unusual type, and the conditions of crystallization are unknown, the results will not be discussed except those for phosphate and carbonate.

Discussion of Results

From the analytical data it appears that on the crystallization of silicates from the magma, germanium is enriched relative to silicon, in olivines (isolated tetrahedra or "nesosilicates"), and pyroxenes (silicate chains or "inosilicates"), but is impoverished in feldspars and quartz (silicate networks or "tectosilicates"). This confirms Wickman's original hypothesis.

This effect does not cause a noticeable enrichment in any one stage of magmatic

differentiation, since the ferro-magnesian minerals and plagioclases usually crystallize at the same time, their respective enrichment factors nullifying each other. This is confirmed by the lack of change in germanium content from rock (original magma) to glass (magma after some crystallization), all these changes being well within the limits of experimental error.

Table 4

	Ge *content* (*p.p.m.*)	
		mean
Rock	0·77 0·91	0·84
Olivine	1·06 1·07	1·06
Biotite	1·26 1·37	1·31
Magnetite	0·75 0·65	0·70
Apatite	0·16 0·18	0·17
Carbonate	0·38 0·39	0·38

Olivine and Pyroxene

Both neso- and inosilicates and perhaps phyllosilicates (using the nomenclature of Strunz), are about equally enriched in germanium relative to silicon, on crystallization from a magma. The enrichment factor seems similar for clino- and orthopyroxenes. With decrease in basicity of the magma, not only do the enrichment factors increase, but also the pyroxene which earlier had the higher factor, becomes relatively less enriched than olivine. It may be that the great increase in Fe^{2+} content in the olivines of the most acid rocks, in causing an expansion of the olivine lattice, will allow the more ready substitution of silicon by the larger Ge^{4+} ion. (The fayalite unit cell is 7% larger by volume than that of forsterite.) This effect would be less evident in the pyroxenes, since, as shown by the chemical analyses of the minerals (Harris, 1952) and by the data of Ramberg and De Vore (1951), the replacement of magnesium by iron is less in pyroxene than in olivine from the same rock, this being particularly evident in acid rocks of low magnesium content.

An alternative explanation for the enhanced enrichment of germanium in the olivines and pyroxenes of the most acid rocks is offered by the structure of the parent liquid. It is known that in silicate liquids the structures, though disordered, resemble closely those of silicate crystals of the same composition (Barth and Rosenqvist, 1949). This similarity is reflected in the low entropy of fusion of silicates. In passing from basic liquids high in iron, magnesium, and calcium, to acid liquids high in silicon and aluminium, the structural units will be built up from small silicate fragments, perhaps consisting largely of isolated silicate

tetrahedra to large units of network type (Richardson, 1948; Bockris *et al.*, 1952).

In the crystallization of olivine from a basic liquid consisting of olivine type units, there will be little enrichment of germanium in the crystal phase, but in olivine from an acid liquid of network type units, there will be a considerable germanium enrichment. In other words, the competition of germanium ions with silicon ions for positions in a nesosilicate lattice will be greater if the germanium is in an unfavourable environment in a network type liquid (i.e., an acid magma) than if it is in a more favourable environment (i.e., a basic magma of silicate units of less complexity).

The same effect of enrichment in the crystal phase in the presence of an acid magma of complex silicate structure is shown in the germanium content of the magnetites.

Feldspar

All the pure feldspars investigated were plagioclases, and in all these germanium is uniformly impoverished, relative to the parent liquid, and the other silicate phases. All but one of the quartz-feldspar mixtures show an even greater impoverishment.

In the pitchstone of Judd's No. 1 Dike, a fraction (*B*) containing plagioclase, orthoclase and quartz was analysed and this shows some enrichment of germanium. Assuming the fraction to contain about 25% of orthoclase, and the rest to be quartz, plagioclase, and minor glass, it would seem that orthoclase might be enriched by a factor as much as two. However, the assumption is based on one analysis of impure material and requires confirmation. It is of interest to note that Goldsmith (1950) in the synthesis of germanium feldspar analogues, found that though $KAlGe_3O_8$ and $NaAlGe_3O_8$ were stable, the pure end member $CaAl_2Ge_2O_8$ was unstable, indicating that germanium substitution might occur more readily in orthoclase than in plagioclase.

Phosphate and Carbonate

The almost negligible Ge contents of the apatite and carbonate phases of the aillikite are noteworthy. Germanium would not be expected to substitute for the carbon atom with its three coplanar bonds in carbonates but the tetrahedral phosphate and silicate groups have sufficient resemblance to expect some germanium substitution there. That germanium does not do so, is explained perhaps by the difference in size of P^{5+} (0·35Å) and Ge^{4+} (0·53Å) ions.

Magnetite and Ilmenite

Though the magnetite and ilmenite fractions were impure, containing up to 10% of silicates (probably olivine and/or pyroxenes), this is not sufficient to account for all the germanium content, and one must assume that germanium is able to enter the magnetite lattice. The relative sizes of the ions, Ge^{4+} (0·53Å), Fe^{2+} (0·74Å) and Fe^{3+} (0·64Å) (using Ahren's, 1952 values for ionic radii) suggests that any substitution of germanium would be for Fe^{3+}. The non-substitution of germanium for Ti^{4+} (0·68Å), as shown by the single ilmenite analysis, must be accounted for by

the increased size and co-ordination number of the Ti^{4+} ion. In magnetite, the Fe^{2+} ions occupy octahedrally co-ordinated positions in the lattice, the Fe^{3+} ions being divided equally between tetrahedral and octahedral positions (i.e., the anti-spinel structure), while in ilmenite, both Fe^{2+} and Ti^{4+} ions occupy octahedral positions in the lattice. With a radius ratio of 0·38 compared with oxygen $\left[\frac{(Ge^{4+})}{(O^{2-})}\right]$ germanium would be tetrahedrally co-ordinated and could replace the tetrahedral Fe^{3+} ion, but would not be expected to occupy an octahedral position so readily.

In the magnetites as in the olivines and pyroxenes the germanium content increases with increasing silica content (and hence complexity of silicate linkage) of the magma.

	Ge content of magnetite	*SiO_2 content of rock*	*Fe_2O_3 content of rock*
Dacite	1·0 p.p.m.	64·8%	1·67%
Pitchstone	1·4 p.p.m.	66·5%	1·43%
Pitchstone	2·5 p.p.m.	71·9%	0·42%
Pitchstone	2·4 p.p.m.	73·2%	0·36%

That is, with increasing complexity of silicate linkage, the germanium has an increasing tendency to escape to another environment—the magnetite lattice.*

Conclusions

The results of the analyses, discussed in the previous section, confirm Wickman's supposition that substitution occurs more readily in least-linked silicates (neso- and inosilicates).

In seeking an explanation of this behaviour of germanium the suggestions of preferential substitution in silicates due to Wickman (1943), Ramberg (1952) and Shaw (1953) may be considered.

Wickman suggests that if the linkages between the silicate tetrahedra are mainly covalent, then the resonance energy will be greater, the greater the degree of linkage. These covalent bonds are weaker for germanium than silicon, so that the difference between the two will increase with the degree of complexity of the linkage and its increasing resonance contribution. Consequently germanium will be relatively enriched in the least-linked mineral, where the difference in bond strength of germanium and silicon is least.

Shaw shows that in ideal cases, isomorphous replacement is dependent on the appropriate solid-solution phase-rule system, which is calculable with a knowledge of the melting points, and heats of fusion of the end members of the system.

* Alternatively the increase in germanium content of the magnetites of the acid rocks might be related to the corresponding decrease in the total amount present of magnetite or potential magnetite, as shown by the Fe_2O_3 content, so that the total amount of germanium present in the magnetite phase of each rock would be about the same. However, in considering the distribution between two lattices (a crystal and a liquid structure), it is probable that one should treat them as two immiscible phases, in which case the distribution coefficient $\left(= \frac{\text{concentration in one phase}}{\text{concentration in other phase}}\right)$ is a function of concentration alone, and is independent of the amount of each phase present, so that this argument would not be valid.

Unfortunately thermal data for the germanium analogues of neso- and inosilicates do not appear to be available. The values of Goldsmith (1950) for the melting points of the appropriate tectosilicates end-members are given.

	M.P.°C	
$NaAlSi_3O_8$	1,118	
$NaAlGe_3O_8$	1,067	
$KAlSi_3O_8$	1,170	(incongruent)
$KAlGe_3O_8$	1,122	
$CaAl_2Si_2O_8$	1,553	
$CaAl_2SiGeO_8$	1,465	

From the plagioclase and orthoclase melting points one would expect impoverishment of germanium on crystallization of these minerals. The estimation of only one potash-containing material is too uncertain to permit any deductions concerning the non-agreement of the analytical and thermal results for orthoclase, while the thermal and analytical material for plagioclase are in good agreement.

A more fundamental, though as yet tentative approach, is that of Ramberg, who relates preferred substitution to the character of the silicate structure itself, and in particular to the nature of the Si-O bond. In the series nesosilicate-inosilicate-phyllosilicate-tectosilicate, the oxygen atoms become progressively more electronegative, and the cation preferred increasingly electropositive.

The argument is developed primarily for the metallic constituents in co-ordinated positions in the silicate lattices, but is extended to the replacement of silicon by aluminium. Ramberg considers that aluminium (electronegativity 1·5) being more electropositive than silicon (1·8) will be increasingly preferred to silicon through the series nesosilicate to tectosilicate.

This argument should be equally applicable to the substitution of germanium (electronegativity 1·7, according to Fyfe (1951)), and the preferential substitution of silicon by germanium should resemble that by aluminium. In fact, as we have seen, the reverse holds true, and germanium substitutes preferentially in neso- and inosilicates.

Finally, the importance should be emphasized of the nature of the silicate liquid or magma in influencing element distribution. The distribution should not be thought of as being a function of crystal lattices alone, without reference to the parent liquid. In crystals in a magmatic solution, the germanium distribution will not depend solely on the relative strengths of the Ge-O and Si-O bonds or other lattice properties, but rather on the relation of these properties to those in the liquid structure. As the structure of the liquid varies with composition, so will the distribution ratios of the substituting elements. That is, the crystallization and composition of minerals will depend not only on their structures and on the concentration of their ions in the parent liquid, but also on the actual nature of the liquid itself.

It is probable that for other solvents, completely different germanium/silicon ratios would obtain on crystallization, and indeed the remarkably high germanium

contents of topaz and other pneumatolytic minerals might be accounted for by the crystallization of the minerals from aqueous rather than siliceous fluids.

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Book review

Gmelins Handbuch der anorganischen Chemie. 8 Auflage, System-Nummer 9 Schwefel, Teil A, Lief. 2. Vorkommen-Technologie des Schwefels und seiner Verbindungen-Kolloider Schwefel-Physiologische Schädigung. Herausg. Gmelin-Institut, Clausthal-Zellerfeld. Verlag Chemie, Weinheim, 1953, 510 S. Preis: DM 244.

Von der vorliegenden Lieferung ist für den Leser dieser Zeitschrift vor allem der Vorkommensteil wichtig. Er umfasst 138 Seiten. Davon sind 7 Seiten dem ausserirdischen Vorkommen gewidmet und 87 Seiten der eigentlichen Geochemie. Der Rest verteilt sich auf eine topographische Übersicht über die Lagerstätten von gediegen Schwefel und Schwefelkies (34 Seiten) nebst einer mineralogischen Beschreibung der Schwefelmodifikationen und der Eisensulfide (10 Seiten). Der Hauptteil des Buches ist also der Technologie des Schwefels gewidmet.

Bei der Behandlung der Geochemie des Schwefels werden zunächst kristallchemische Grundlagen und eine Übersicht über die Verbreitung und geochemisches Verhalten gegeben. Es schliessen sich die Abschnitte über die magmatische, sedimentäre und metamorphe Abfolge an. Auf die Behandlung der Lithosphäre folgt dann die der Hydrosphäre, Atmosphäre und Biosphäre. Die Gliederung bringt für den Unerfahrenen, wie auch in anderen Bänden, einige Überraschungen. So werden z.B. die rezenten Meeressedimente bei der Hydrosphäre und die Böden nicht im Anschluss an die Verwitterung sondern an die Biosphäre behandelt. In den geochemischen Abschnitten werden vor allem Schwefel und Schwefelkies behandelt. Die gesamten Sulfatlagerstätten der Erde findet man in wenigen Zeilen bei der Verwitterung erwähnt, was wohl damit zusammenhängt, dass sie im Band Kalium desselben Handbuchs ausführlicher behandelt worden sind. Besondere Aufmerksamkeit ist dem organischen Kreislauf des Schwefels gewidmet, sowohl in dem Abschnitt über Kaustobiolithe bei den Sedimenten wie in dem Abschnitt über die Biosphäre.

Der Arbeitsgemeinschaft dieses Teils, die 9 Namen umfasst, muss man für die eingehende Durcharbeitung der Literatur sehr dankbar sein. Der alte Wunsch, dass die Bearbeiter der einzelnen Teile angegeben werden, ist auch in diesem Band nicht erfüllt worden. Der sehr hohe Preis wird allerdings die Anschaffung nur wenigen ermöglichen.

C. W. Correns.

NOTICE

South African National Committee on Geochronology

The above Committee, which has recently been formed under the sponsorship of the South African Council for Scientific and Industrial Research, wishes to make known the fact of its existence. This Committee was called into being "to take note of developments in this field in South Africa and overseas and to do all it can to further them."

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AHRENS, L. H. (1952) Geochim. et Cosmochim. Acta, 2, 168.

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6. To conserve space authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

DEEP-SEA RESEARCH

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